FINAL REPORT ON CHEMICAL AND THERMAL ANALYSIS

CAPP/T F
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by TRI

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SYNOPSIS

Work during the past three years has included significant research in several areas aimed at further clarification of the aging and chemical failure mechanism of thermoplastics (PVDF or Tefzel) for pipes. Among the areas investigated were the crystallinity changes associated with both the Coflon and Tefzel after various simulated environmental exposures using X-Ray diffraction analysis. We have found that significant changes in polymer crystallinity levels occur as a function of the exposures. These crystallinity changes may have important consequences on the fracture, fatigue, tensile, and chemical resistance of the materials. We have also noted changes in the molecular weight distribution and the increased crosslinking of the Coflon material using Gel Permeation Chromatographic Analysis. Again these changes may result in variations in the mechanical and chemical properties in the material. We conducted numerous analytical studies with methods including X-ray Diffraction, Gel Permeation Chromatography, Fourier Transform Infrared Spectroscopy, and Differential Scanning Calorimetry. We investigated a plethora of aged samples of both Tefzel and Coflon that were forwarded from MERL. Pressurized tests were performed on powdered PVDF in a modified Fluid A, which we will call A-2. In this case the ethylene diamine concentration was increased to 3 percent in methanol. Coflon pipe sections and powdered Coflon were exposed in pressure cells at 1700 psi at three separate test temperatures.

1.0 X-RAY DIFFRACTION ANALYSIS OF AGED COFLON AND TEFZEL

X-ray Diffraction was conducted on both samples from the exposed Tefzel and Coflon thermoplastics. The exposure fluids for the environmentally aged samples are detailed below.

Clearly, all of the exposures for both materials had an effect on the percentage crystallinity. The greatest decrease in crystallinity for both polymers was observed with the Tefzel Fluid G exposure in methanol with ethylene diamine. We also note that the percentage of crystallinity for Coflon increases or decreases depending on the exposure. The results from the X-ray diffraction testing are contained in CAPP documents.

(1) Fluid A- 100% Methanol
(2) Fluid B- 97/3 CH4/CO2 with saturated water vapor
(3) Fluid C- 97/3 CH4/CO2
(4) Fluid D- 94/5/1 CH4/CO2/ H2S
(5) Fluid E- 94/5/1 CH4/CO2/H2S with saturated water vapor
(6) Fluid F- As fluid E plus 1% ethylene diamine
(7) Fluid G- As fluid A plus 1% ethylene diamine
(8) Fluid H- As Fluid B plus 1% ethylene diamine
(9) Fluid I - Hydrocarbon mixture, synthetic
(10) Fluid J - 9911 distilled water 1 ethylene diamine

In general the Coflon samples are more crystalline. Table 1-1 shows the results of the analysis including the fluids the samples were exposed to prior to testing. Color changes were apparent with both the Tefzel and Coflon materials after exposures, the darkest Coflon material had the lowest level of crystallinity.

The percent crystallinity is calculated as the integrated area of the crystalline portion of the X-Ray diffraction pattern, as determined after background removal, divided by the total integrated area of the patterns. Correction factors for air scattering are also applied.

Included in Table 1-2 are the percent (%) crystallinities on three powdered Coflon samples. Three samples are Coflon Baseline Powder (CBP) (unaged), CP70 (aged at 70°C) and CP110 (aged at 110°C), and CP130 (aged at 130°). The results on four powder samples, three aged in the Atlas cell, are shown below in Table 1-2. The results show a decrease in crystallinity after aging.

Table 1-1. Results Of The X-Ray Diffraction Analysis Including The Fluids The Samples Were Exposed To Prior To Testing

Control Tefzel	White	26.0%	Laboratory Temperature and Conditions
T-29 Tefzel	White	25.6%	Fluid A, 6 days 140 °C vapor pressure
T-50 Tefzel	White	22.9%	Fluid F, 120° C 5kpsi 4 weeks
T-57 Tefzel	White	20.5%	Fluid E, 120° C 5kpsi 4 weeks
T-59 Tefzel	White	1.7%	Fluid G, 120° C 5kpsi 4 weeks
T-105 Tefzel	White	9.0%	Fluid A, 6 days 140°C vapor pressure
Control Coflon	White	41.5%	Laboratory Exposure and Conditions
T-31 Coflon	White	34.0%	Fluid A, 13 days 140 °C vapor pressure
T-43 Coflon	Brown	39.9%	Fluid F, 120° C 5kpsi 4 weeks
T-56 Coflon	White	45.6%	Fluid E, 120° C 5kpsi 4 weeks
T-58 Coflon	Brown	11.5%	Fluid G, 120° C 5kpsi 4 weeks
T-73 Coflon	Beige	39%	Fluid F, 3 months 100° C
T-74 Coflon	Beige	35	Fluid F, 120° C, 2 weeks
T-75 Coflon	Beige	31% prev. 26%	Fluid F, 140° C 3 days
T-76 Coflon	Beige	27.2	Fluid F 140 °C 5 days
T-77 Coflon	Beige	34% prev. 29%	Fluid E, 140° C 8 days
T-87 Coflon	White	40%	After 27 days at 120-130° C in air oven
T-90 Coflon	Beige	29% prev. 39%	Fluid F, 140° C 5 ksi 2 weeks
T-91 Coflon	Beige	37%	Fluid F, 140° C 5 ksi 4 weeks
T-100 Coflon	Brown	39%	Fluid G, 65° C, reflux 2 weeks
T-66 Coflon	Beige	25.5	Fluid A 120 °C 22 days
T-68 Coflon	Beige	29.1	Fluid A 120 °C 126 days
T-79 Tefzel	White	18.0	Fluid F 100 °C 1 month
T-84 Tefzel	White	20.2	Fluid F 140 °C 8 days
T-88 Coflon	Beige	42.0	Fluid F 120 °C 1 week
T-89 Coflon	Beige	41.0	Fluid F 120 °C 3 week
T-102 Coflon	Beige	48%	Fluid I, 140° C, 5 ksi 10 weeks

Table 1-2. Percent Crystallinity Results for Coflon Powder Samples

Sample	% Crystallinity	Exposure
CBP	41%	Laboratory Ambient
CP70	37%	Fluid G2 70°C 1 week
CP110	32%	Fluid G2 110°C 1 week
CP130	18%	Fluid G2 130°C 1 week

The changes in crystallinity were used to construct an Arrhenius relationship as displayed in Figure 1-1. An activation energy of 3 kcal/mole was obtained for the process. This is a rather low activation energy indicating that the energy needed to initiate the degradation reaction is relatively small. Likewise, within the range tested, the effect of temperature on acceleration of the process is also relatively small.

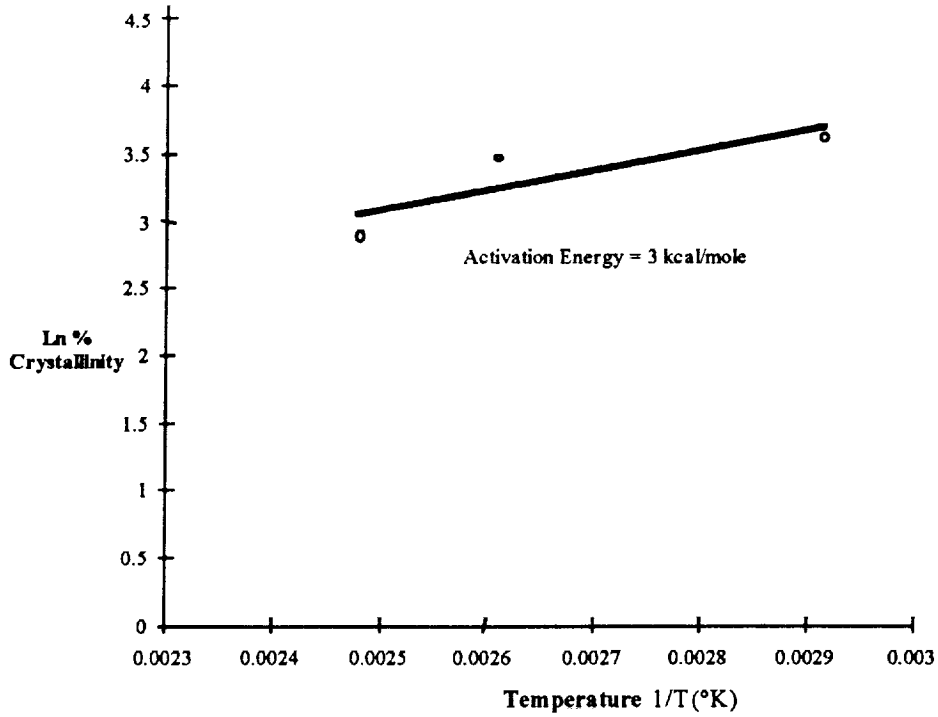

Figure 1-1. Plot Of Arrhenius Relationship Of Aged Coflon Powder

We attempted to model the data considering the decrease in crystallinity to be a first order reaction. The reaction rate was taken to have an Arrhenius temperature dependence. With the data available this led to three equations and three parameters, two of which were known previously. The three equations were solved for the third parameter leading to three fairly different values for the reference reaction rate. We concluded that the model considered did not constitute an adequate representation of the data. In order to further define the mechanism additional testing at other temperatures will be needed.

The most interesting result of this x-ray powdered Coflon analysis was the fact that, in addition to crystallinity changes upon heating, a structural change is also observed upon heating. The raw data composite plot containing the baseline, 70°C, and 110°C Coflon powder shows the peak shift occurring at the higher 2θ range (lower d-spacing). In Table 1-3 we see the d-spacings in this region increasing upon heating.

Table 1-3. Shifted Peak D-Spacing For Coflon Powder Samples

Sample	D-Spacing for Shifted Peak	Δd
CBP	2.19A	
CP70	2.20A	+0.01 A
CP110	2.25A	+0.05A
CP130	Peak Not Significant	+0.05A

In the 2θ range between 15° and 35°, the peak positions remain stationary. The 2θ range between 35° and 60°, however, shows significant peak shifts to lower d-spacings upon heating. The 2θ range below 5° shows a large peak developing upon heating to 110°C.

It should be noted that although the bulk of CP130 sample showed less crystallinity and a greater amorphous area, there were tiny individual crystallites identified in this sample (but not in the other samples).

The peak shifts indicate structural changes occurring upon heating. One theory for this is that the peaks between 15° and 35° (stationary peaks) represent regular inter-chain distances which do not change upon heating. In contrast, the region between 35° and 60° represents a secondary structure based upon the dipole moment (and arrangement) of the fluorine atoms. These bonds have a typical disassociation energy of between 1.5 to 3 kcal/mole. The shift to higher d-spacing appears to be related to an increase in chain length, (or increase in distance between chain folds in the structure of the polymer) caused from the relaxing of the interchain or intrachain structure, in a way similar to a compressed spring relaxing. Notice that the intensity of the peaks in this region also decrease, which also indicates a decrease in crystalline structure associated with these d-spacings. From the X-Ray diffraction pattern in the region between 35° and 65° 2θ, we see both a chain length increase from the peak position change and a decrease in crystalline structure from the decrease in peak intensity.

Coflon Pipe Tube Cross Section

X-Ray diffraction patterns were taken by stepping from the outer to the inner wall of the tube cross section. The tube cross section wall thickness is 8 mm. The percent crystallinity results are shown in Table 1-4.

Table 1-4. Percent Crystallinity Through a Coflon Pipe Section

Location on Sample	% Crystallinity	Exposure
1 mm from outside	37%	Laboratory Ambient
3 mm from outside	9%	Laboratory Ambient
4 mm from outside	11%	Laboratory Ambient
6 mm from outside	15%	Laboratory Ambient
8 mm from outside	18%	Laboratory Ambient

The crystallinity is highest at the extreme outer wall. It falls off quickly and then increases slowly to the inner wall.

Again, we are seeing structural changes as well as crystallinity changes over this cross section. The pattern taken at the extreme outer wall of the tube shows a

completely different and more ordered structure, as seen by the crystalline peaks emerging between 35° and 60° 2θ. This increased order could be due to differences in the fluorine dipole moments and atomic arrangement as discussed in the section above. The amorphous scattering is also increasing as shown by the increasing background intensity.

This experiment represents a classic skin-core X-Ray diffraction result. It does suggest that the structural change is due to a difference in the cooling rate between the two walls.

2.0 COFLON ESCA RESULTS

Two specimens were tested using ESCA, unaged and aged in 5% H_2S at 140°C 1000 psi for 7 days with no permeation exposure. Table 6-2 shows these results. A dramatic decrease in fluorine is seen after aging accompanied by an increase in sulphur content. This agrees with the FTIR results that indicate unsaturation resulting from loss of HF followed by sulphide crosslinking.

Interestingly, there was also a substantial increase in oxygen observed in the aged specimen. This may be due to oxidation occurring after the aged specimen was exposed to ambient atmosphere or may be a result of adsorbed moisture adhering to the aged surface that is likely to be more hydrophilic than the unaged material.

3.0 GEL PERMEATION CHROMATOGRAPHY OF AGED COFLON

Gel Permeation Chromatography was conducted on a number of environmentally aged Coflon test pieces. The solvent was NMP and the flow rate was 6mL/ minute. The injection volume was 100 uL the detector temperature was set at 35°C and the columns were run at 80°C.

A model 200 Viscotek GPC was used for the analysis with a refractometer/ viscometer dual detector system.

A Viscotek Universal detection system was used for the analysis. This consists of a refractometer and a wheatstone bridge type viscometer. The molecular weight is calculated via the Universal Calibration Technique. This allows us to measure absolute molecular weight and molecular size independent of the polymer calibration type.

The moderate intrinsic viscosity values coupled with the linear Mark-Houwink plots (over most of the molecular weight range) present in these samples indicate that Coflon samples have generally a linear structure. By further examination of the Mark Houwink plots there is a crosslinked or aggregated material present at the high end of the molecular weight. This is more prominent in materials having a darker color and decreased solubility. Sample T-58 showed the highest amount of this high molecular weight material and the lowest dissolution percentage. All of the samples have a high z- average molecular weight because of this phenomenon.

Table 2-1. Gel Permeation Chromatography

Molecular Weight Distributions				
Sample ID	Mn	Mw	Mz	Exposure
Control Coflon	81,700	538,900	3,217,000	No Exposure
T-31 Coflon	92,900	636,100	2,060,000	Fluid A 140°C 13 days
T-43 Coflon	81,100	779,500	10,600,000	Fluid F 120°C 4 weeks
T-56 Coflon	80,700	461,200	2,403,000	Fluid E 120°C 4 weeks
T-58 Coflon	44,300	3,742,000	143,940,000	Fluid G 120°C 4 weeks
T-68	115,400	379,600	814,500	Fluid A 120°C 126 days
T-70	101,900	350,300	762,800	Fluid A 100°C 126 days
T-72	85,600	332,800	784,400	Fluid F 100°C 1 month
T-73	105,300	281,800	503,100	Fluid F 100°C 3 months
T-7D70	115,800	310,500	606,900	Fluid G2 70°C 1 week
T7D110	116,000	285,400	497,800	Fluid G2 70°C 1 week
T-75 Coflon	177,460	536,509	1,062,095	Fluid F, 140¡C 3 day
T-77 Coflon	170,504	532,717	1,052,564	Fluid F 100°C 8 days
T-74 Coflon	152,905	534,361	1,080,943	Fluid F 120°C 2 weeks
T-87 Coflon	171,265	538,897	1,067,315	Air 120°C-135°C oven 27 days 120-135°C air oven
T-88 Coflon	177,880	549,827	1,084,282	Fluid F, 120°C 5 ksi 1 weeks
T-89 Coflon	173,803	539,103	1,073,977	Fluid F, 120°C 5 ksi 3 weeks
T-76 Coflon	173,329	534,908	1,059,213	Fluid F 140°C 8 days
T-53 Coflon	158,990	519,823	990,690	Fluid F, 120°C 5 ksi 4 weeks gas phase

Comparisons of samples structure may be made by overlaying Mark-Houwink plots. Samples Coflon standard, T-31 Fluid A, T-56 Fluid E, T-60 Fluid H all have very similar structural characteristics. The downturn of the Mark-Houwink plot at the higher molecular weight represents the crosslinked or aggregated material. Up to approximately one million molecular weight the Mark-Houwink slope is 0.7 which is representative of a linear structure. Beyond this point the slope quickly approaches 0 indicating a hard sphere model.

By overlaying the other materials (using Coflon Standard as the reference) we find deviations specifically in the high end of the material. The noise on the T-58 sample is high due to the fact that there seem to be multiple aggregate peaks and an overall low dissolution value. There is a great deal of material in the high molecular region for the T-58 sample.

Finally, by overlaying the Mark-Houwink plots of the two T-43 runs, one sample was dissolved at 180°C while the other was dissolved at 100°C, we can see that the highly heated sample is crosslinked or aggregated throughout the distribution.

A universal calibration detector system was used for the analysis. This consists of a refractometer, and viscometer combination. Concentration distribution was calculated through the refractive index signal, and the viscosity was calculated directly through the Differential Wheatstone Bridge Viscometer. The molecular weight is calculated via the Universal Calibration technique. This allows us to measure absolute molecular weight and molecular size independent of the polymer calibration type.

The universal calibration curve is given with the viscometer chromatogram overlaid in Figure 3-1. The maximum error based upon the standards is 8.0% and the average error is 4%

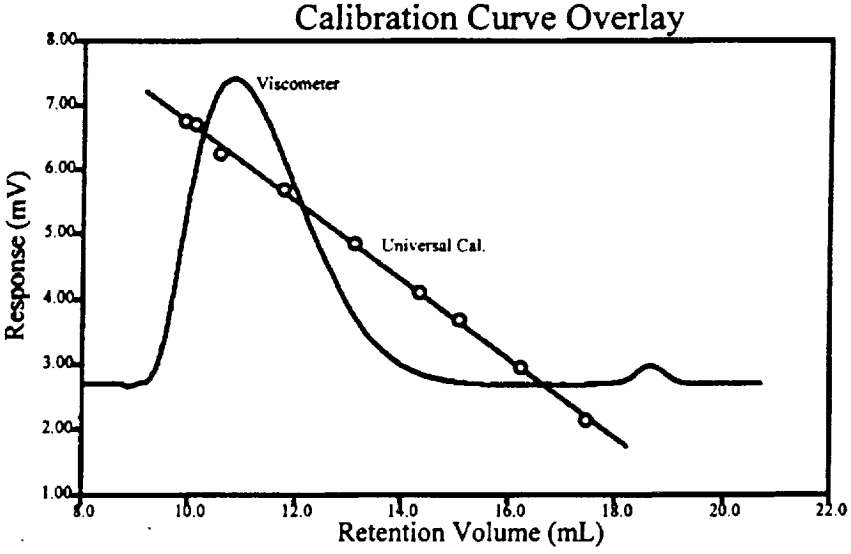

Figure 3-1. GPC Calibration Overlay

Signal to noise was excellent on the Viscometer. There was some linear drift present on the Refractometer. Despite this drift, the signal to noise was applicable for good Universal Calibration reproducibility and accuracy.

The moderate intrinsic viscosity values coupled with linear Mark-Houwink plots (Figure 3-2) (over most of the molecular weight range) present in these samples indicate that the samples have a general linear structure. (There is no evidence of any aggregated or crosslinked material in these samples that seemed to be present in the first set of samples that was run. However, samples T73, T7D70, and T7D110 had different Mark-Houwink plot than that of samples T68, T70, and T72. This indicates that there is either the presence of a backbone modification or short chain branching difference between these samples, or that there is the presence of a contaminant in one of the two sample lots as shown by the Mark-Houwink Plot

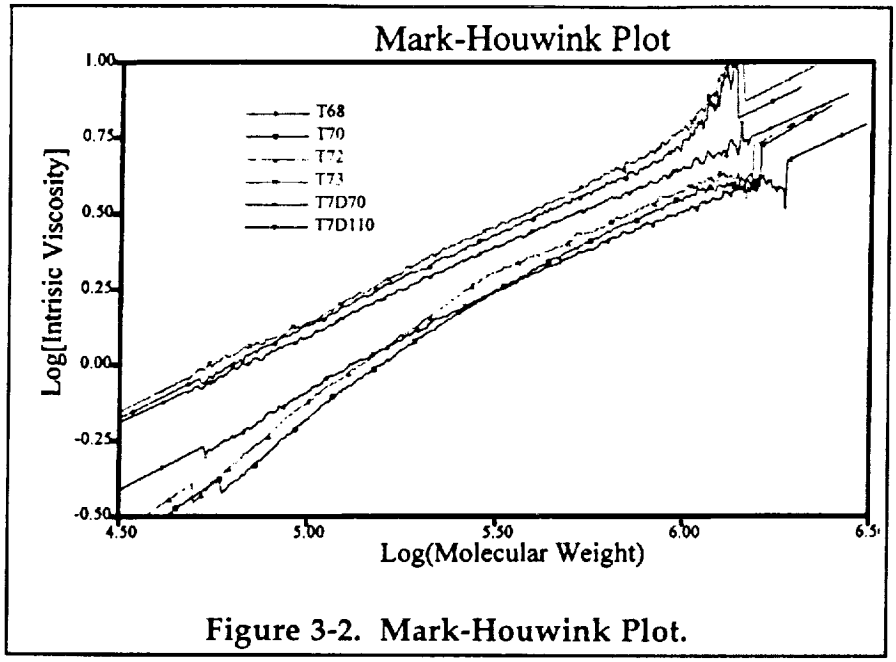

Figure 3-2. Mark-Houwink Plot.

Samples run in duplicate gave similar findings. As in the case of the previous samples, dissolution percentage varied between sample lots with the worst recovery (estimated between 40-50% from samples T68, T73, T7D70, and T7D110. Later samples were run on a Waters 150 high temperature gel permeation chromatograph making use of information concerning the hydrodynamic volume from the previous viscometric analysis.

Overlaying these samples (Figure 3-3) with the past samples that were run, confirms no aggregation compared to samples T73, T7D70, and T7D110. Samples T68, T70, and T72 seem to be different in structure somehow (i.e.) less compact or lighter on the backbone.

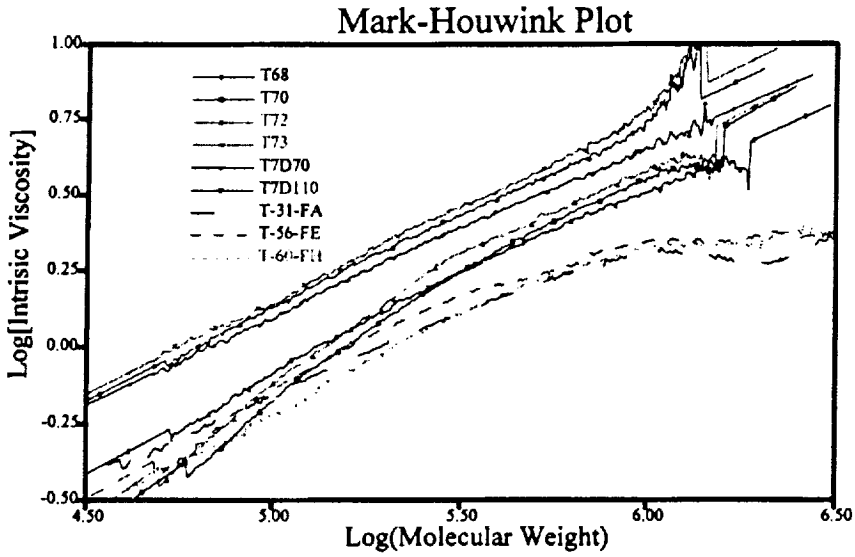

Figure 3-3. Mark-Houwink Plot Overlaid with previous samples.

4.0 ELEMENTAL ANALYSIS

Elemental Analysis was conducted on samples throughout the three year project. Substantial changes in elemental composition were noted particularly for Coflon as a function of exposure. The change in elemental composition of the Coflon materials lends support to the idea of dehydrohalogenation under certain environmental conditions. Table 4-1 summarizes the elemental analysis results.

Two samples. T79 and T92 showed (initial results) total percentages (CHNF) of <95%. Carbon results were confirmed in reanalysis. Repeating fluorine using a smaller sample size on some samples resulted in a correspondingly greater value such that total percentages showed >99%. Fluoride analysis was conducted using a ion specific electrode. Fluorine recovery tended to be more difficult in the analysis. There are several samples (T68, T76, T85) whose total percentage values are <99%. The fluorine value is slightly low due to some incomplete recovery of fluorine. Combustion difficulties also can result in slightly excessive nitrogen. Values greater than 0.1 are suspect. Reanalysis of samples whose initial nitrogen is >0.2 usually resulted in a lower value. We have not reanalyzed T76 and T86. The nitrogen value for T92 was the only one which consistently showed >0.3%.

5.0 SCANNING ELECTRON MICROSCOPY (SEM) AND X-RAY ANALYSIS OF AGED COFLON

Scanning Electron Microscopy was performed on aged (5% H2S 7 days 130°C, methane permeation at 2500 psi and 130°C) Coflon samples. The results are detailed in previous CAPP reports. The results provided a visual and chemical mapping through the bulk of the samples. Videotaping of the SEM samples was also performed. The analysis was conducted using a Amray 1820 Scanning Electron Microscope interfaced with a Kevex Multichannel Analyzer for elemental detection and mapping.

The micrographs indicate an extremely smooth surface for the unaged Coflon material. Micrographs at the same magnification indicate a crater filled cavernous surface with the aged Coflon material. The topography extends throughout the thickness of the sample not just on the surface. This is similar to the surfaces observed when PVC is aged and embrittled after long term outside aging.

The x-ray analysis of the aged sample indicates the presence of a high level of Sulfur and smaller amounts of Calcium, Zinc, and Silica. The calcium and zinc could be involved in the stabilizer package for the polymer. The silica is probably from some dust contamination of the surface. No fluorine peak is evident in the aged Coflon sample, it is lost in the baseline. The unaged x-ray analysis indicates a very strong absorption of Fluorine in the spectrum. No other elements are obvious in the spectra of the unaged Coflon Sulfur can shield the fluorine peak, however, it is surprising to see such a strong peak totally absent in the aged specimen. A tremendous decrease in the fluorine content on the surface of the aged Coflon was observed (by ESCA).

Table 4-1. Elemental Analysis of Coflon and Tefzel Samples

Sample ID	%C	%H	%N	%F	Exposure
CBP Coflon	40.77	3.91	<0.02	54.64	Ambient Baseline Powder
T-66 Coflon	37.91	3.13	<0.02	59.05	Fluid A 120 °C 22 days
T-68 Coflon	38.01	3.09	0.08	56.88	Fluid A 120 °C 126 days
T-74 Coflon				57.13	Fluid F 120°C 2 weeks
T-75 Coflon				56.82	Fluid F 140°C 3 days
T-77 Coflon				56.42	Fluid F 140°C 8 days
T-89 Coflon				57.30	Fluid F 120°C 5 KSI 3 weeks
T-88 Coflon				56.78	Fluid F 120°C 5 KSI 1 week
T-72 Coflon	39.96	3.48	0.09	56.26	Fluid F 100 °C 1 month
T-76 Coflon	40.06	3.65	0.19	54.20	Fluid F 140 °C 5 days
T-79 Tefzel	36.30	2.75	0.03	60.29	Fluid F 100 °C 1 month
T-84 Tefzel	36.52	2.80	<0.02	60.55	Fluid F 140 °C 8 days
T-85 Coflon	40.63	3.82	0.11	53.79	Unaged
T-86 Coflon	40 49	3.75	O.22	55.45	Unaged extruded bar
T-91 Coflon	38.04	3.24	0.15	58.62	Fluid F 140 °C 5ksi 4 weeks
T-92 Coflon	38.31	3.35	0.32	58.12	Fluid G 120 °C 5ksi 2 weeks
CP70 Coflon	37.23	3.10	0.08	58.62	Fluid G2 70 °C 1 week
CP110 Coflon	37.72	3.04	0.07	59.61	Fluid G2 110 °C 1 week
CP130 Coflon	49.72	4.30	7.29	36.98	Fluid G2 130 °C 1 week
T-9 Tefzel	36.19	2.80	0.00	61.07	8 days methanol, 140°C, unstrained 5 ksi
T-19 Tefzel	36.54	2.86	0.00	61.04	14 days methane, 140°C, strained 7% 5 ksi
T-7 Coflon	37.87	3.33	0.01	58.40	14 days Nitrogen, 140°C, 7.5% strain
T-8 Coflon	37.54	3.29	0.01	58.82	14 days methanol, 140°C, 7.5% strain, 5 ksi
T-12 Coflon	38.12	3.28	0.01	58.95	8 days methanol, 140°C, unstrained reached 170°C
T-23 Coflon	37.62	3.29	0.01	58.86	14 days methanol, 140°C unstrained, 5 ksi
*Aged Coflon	71.47	11.47	0.00	<0.03	5% H2S 7 days, 130°C, methane permeation 2500 psi and 130°C, amine vapor.
T-28 Coflon	37.74	3.23	0.01	58.99	
T-29 Tefzel	37.18	2.75	0.05	59.61	6 days fluid A, 140°C vapor pressure
T-30 Coflon -White Porous	37.86	3.18	0.03	56.36	13 days Fluid A, 140°C vapor pressure

Table 4-1 (cont'd). Elemental Analysis of Coflon and Tefzel Samples

T-31 Coflon White Porous Foam ≈ 10PCF	38.02	3.13	0.03	58.18	13 days Fluid A, 140°C vapor pressure
T-36 Coflon	58.39	8.55	0.51	11.84	13 days Fluid A, 140°C vapor pressure in glass ended cell, residue from evaporated fluid at end of test
T-41 Coflon Skin - Dark Brown Skin White Inner	41.80	3.42	0.70	52.91	4 weeks Fluid F, 120°C, 5kpsi, tested in gas phase
T-42 Tefzel	36.28	2.71	0.04	60.83	4 weeks Fluid F, 120°C, 5kpsi, tested in gas phase
T-52 Tefzel	36.22	2.81	0.01	60.82	4 weeks (gas phase) Fluid F, 120°C, 5kpsi, subsequent permeation in methane at 140°C 5ksi

6.0 ANALYTICAL DATA USING ESCA AND SEM ELEMENTAL ANALYSIS

In order to substantiate the ESCA, and the x-ray analysis, bulk elemental analysis was performed. The following table compares the elemental analysis results with the ESCA results.

Table 6-1. Elemental Analysis Results For Coflon Elemental Composition Data Measured From The Bulk Interior Of Specimen

Specimen	C	N	H	F		S
(5% H2S 7 days 130°C, methane permeation at 2500 psi and 130°C	71.5	7.3	11.5			1.29
Coflon Control (unaged)	40.7	4.1				<0.1

Table 6-2. ESCA Results For Coflon Elemental Composition Data Measured From The Surface (Approximately The Top 100 Angstroms) Of Each Sample And Expressed In Atomic Percent Units For The Elements Detected.

Specimen	C	N	O	F	Si	S	Fe	Zn
Coflon COF4 Aged in 5% H2S at 140°C 1000 psi for 7 days No Permeation	75	3.1	14	1.6	4.1	1.3	0.5?	0.4
Coflon Control (unaged)	52	—	3.1	44	0.3	0.1?	—	—

Note: ? = weak signal
— = no signal detected

We postulated that the changes were an elimination dehydrohalogenation type mechanism. This reaction occurs either in the presence of bases such as amines or hydroxides. These types of reactions are commonly known to occur with compounds such as PVC. Very little in the literature describes these processes occurring with PVDF. Considering the initial results after only thermal exposures it appears that Coflon and Tefzel are both relatively stable and undergoing no substantial elemental changes or reactions. This indicates that either the aliphatic amine and or the H_2S are essential in addition to thermal activation to produce substantial elemental changes in Coflon.

7.0 THERMAL ANALYSIS

Thermal analysis evaluations were performed on aged and unaged Coflon and Tefzel. These studies examined the effects of chemical aging of these two polymeric materials that are typically used for offshore fluid transport applications. The methods used were:

Differential Scanning Calorimetry (DSC)

This instrument measures heat flow from a sample as a function of temperature for determination of:

- Percent crystallinity via heat of fusion;
- Residual solvents; and
- Change in melt temperature after aging.

Thermogravimetric Analysis (TGA)

For measurement of weight loss and gain of materials with temperature relating to:

- Percent plasticizer;
- Decomposition temperature;

Thermomechanical Analysis (TMA)

For measurement of dimensional changes as a result of temperature:

- Shrinkage from loss of plasticizer;
- Swelling due to solvent swell;
- Coefficient of thermal expansion;
- Glass transition temperature; and
- Stress relaxation.

Dynamic Mechanical Analysis (DMA)

Frequency of oscillation and energy parameters are transformed into mechanical property information as a function of temperature:

- Flexural storage and loss modulus
- Shear storage and loss modulus
- Tan delta (damping factor)

Coflon DSC Results

One of the early evaluations involved the chemical aging of Coflon in H_2S at various temperatures at 1000 psi. The Coflon specimens were cut from pipe sections and exposed at either 100, 120 or 140°C for seven days. One of these specimens was subsequently tested for methane permeation, and another for H_2S permeation.

Table 7-1 illustrates the results for the DSC tests performed on the aged and unaged Coflon specimens. One of the most dramatic comparisons is the difference in melt onset temperature observed with the specimen exposed to methane permeation. This specimen exhibited an onset of 190°C compared to a range of 157 to 167°C for the other cases. In view of the fact that this material also displayed the highest degree of crystallinity it appears that the methane removed amorphous polymer from the specimen surface.

In contrast, exposure to high pressure H_2S produces a lower melt onset and percent crystallinity compared to the unaged material. If sulphide crosslinking is occurring it may result in disruption of crystallinity which would account for this behavior.

Table 7-1. Differential Scanning Calorimetry Results for Coflon

Aging Temperature[1] (°C)	Permeation Conditions	Melt Onset (°C)	Percent Crystallinity
Unaged	None	162	54
100	10% H_2S 130°C 2500 psi 1 day 5000 psi 1 day	157	34
120	methane 130°C 2500 psi 1 day	190	72
140	None	167	41

1 = Aged samples were exposed to 5% H_2S for 7 days at 1000 psi. Specimens were 0.015" shavings from exposed high pressure surface

In a separate experiment a set of PVDF films was prepared for the DSC tests. The films were prepared by casting from DMAC solution. These specimens were exposed to methanol/EDA for 0.25, 1.0, and 15 hours respectively. After exposure, the sections of the films were subjected to Differential Scanning Calorimetry (DSC) testing. Sections were cut from the dry aged films and placed into tarred DSC sample pans. The sample temperature was raised at a constant rate of 10°C per minute to a maximum of 200°C. Melt onset onset, peak temperature, and heat of fusion were thus determined.

Tabular data describing the melt aspects and heats of fusion are shown in Table 7-2.

Table 7-2. Thin Film DSC Results

Coflon Film Sample	Melt Onset (°C)	Melt Peak (°C)	Heat of Fusion (J/g)
Baseline	161.45	173.74	58.49
Aged 0.25 hrs	162.11	177.12	56.89
Aged 1.0 hrs	160.76	174.55	68.21
Aged 15 hrs	153.87	169.39	40.17

A slight increase in melt temperature was noted with the 0.25 hour aged specimen. At the 1 hour and 15 hour exposure level the melting points appear to be decreasing. Most notable are the values obtained from the specimen which was aged 15 hours. Here the melt onset and peak temperatures dropped significantly as did the heat of fusion. This results lends credibility to the hypothesis that initial aging of PVDF in this fluid causes some crosslinking and at longer exposure times lower molecular weight species begin to appear which may lower the melt points and heats of fusion.

After aging in fluids A and B, the DSC results of the Coflon materials indicated considerable variability in crystallinity depending on aging conditions. We generally observed an increase in the heat of fusion as a function of heating time and temperature. Some of this effect may be attributable to the loss of plasticizer. The residue from the evaporated fluid after 14 days exposure to fluid A at vapor pressure indicates the presence of three compounds with vastly different melt temperatures from Coflon. The three compounds are possibly plasticizer, the solvent, and the decomposed polymer. Based on the DSC information we are not observing any change from the α form to the β crystalline form. The β form has a melting point of 190°C. We are clearly observing some changes in the relative amount of crystallinity of the Coflon based upon exposure. The DSC results for the samples, the heat of fusion's, the exposure conditions, and percentage crystallinity are given in Table 7-3.

Table 7-3. Coflon DSC Results After Aging in Fluids A and B

Sample Identification #	Exposure Conditions	Heat of Fusion	Percentage Crystallinity
Coflon Baseline	Not aged	67.59 J/g	64.6%
Tefzel Baseline	Not Aged	39.00 J/g	
T-26 Coflon	14 days Fluid B, 140°C 5,000psi	77.96 J/g	74.5%
T-30 Coflon	13 days Fluid A, 140°C vapor pressure	48.30 J/g	46.2%
T-31 Coflon	13 days Fluid A, 140°C vapor pressure	44.23 J/g	42.3%
T-32 Coflon	13 days Fluid A, 140°C vapor pressure	67.16 J/g	64.2%
T-36 Residue from evaporated fluid at end of test Coflon	13 days Fluid A, 140°C vapor pressure	3 peaks none near the 150-160°C melt onset of Coflon	0
T-29 Tefzel	6 days fluid A, 140°C vapor pressure	51.50 J/g	32.1 % increase in crystallinity over unaged
T-33 Coflon	13 days Fluid A, 140°C vapor pressure	30.54 J/g	29.2%

The DSC results presented in Figure 7-1 show the effects of deplasticization on the melt onset of Coflon. After deplasticization the melt onset increases slightly. Also note in the same figure the effect of aging in EDA/methanol on the melt onset. Particularly after the aging expsoure at 130°C, the melt onset was observed to decrease by about 40°C.

Tefzel DSC Results

The Tefzel specimens as tested consisted of the following:

- Unaged;
- Methanol permeation specimen exposed for 2 days at 100°C and 2500 psi;
- Methanol absorption specimen exposed for 3 days at 150°C and 15 Bar.

Initial Tefzel Methanol Exposures

The Tefzel specimens were cut from 0.05 mm. sheet stock followed by exposure to methanol at elevated temperature and pressure. One of these specimens was exposed to methanol permeation for 2 days at 100°C and 2500 psi. An additional specimen was exposed to liquid methanol for 3 days at 150°C and 15 Bar.

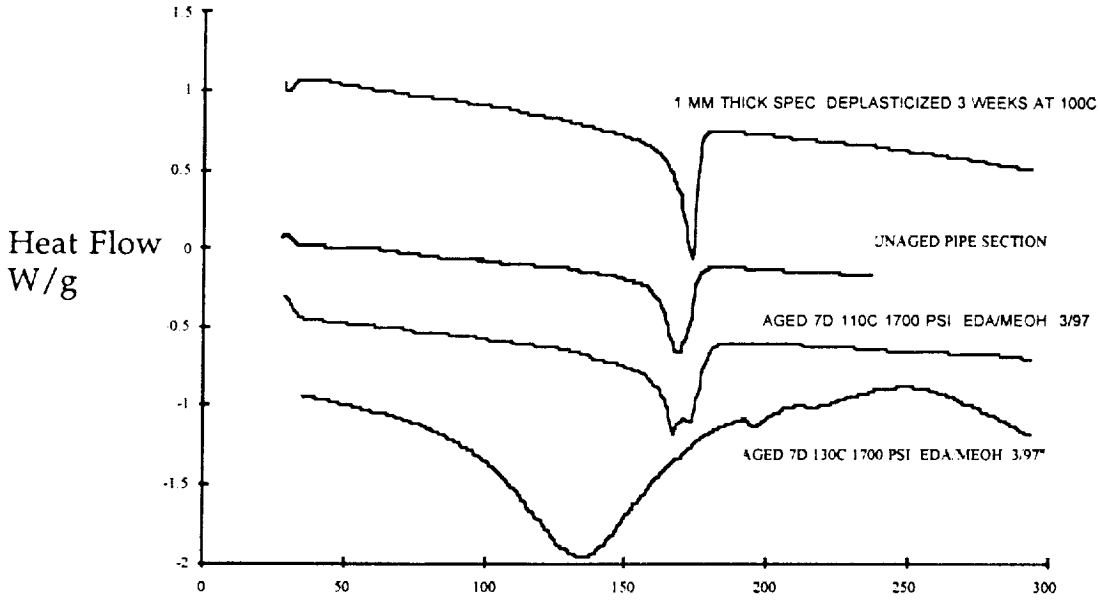

Figure 7-1. DSC Results for Aged Coflon

Melt temperature onsets, shown in Table 7-4, were similar for all of the specimens (252-253°C) with the exception of the low pressure side of the methanol permeation specimen exposed for 2 days at 100°C and 2500 psi. In this case the melt onset was 246°C. The heats of fusion ranged from 39 J/g for the unaged specimen to 75 J/g for the low pressure side of the methanol permeation specimen exposed for 2 days at 100°C and 2500 psi.

The Tefzel specimens were not exposed to H_2S and showed no significant indication of chemical degradation as a result of exposure to methanol at high pressure.

Table 7-4. Differential Scanning Calorimetry Results for Tefzel

Aging Temperature (°C)	Permeation Conditions	Melt Onset (°C)	Heat of Fusion (J/g)
Unaged	None	252	39
150 (methanol, 15 Bar)	None	252	62
	Methanol 2500 psi 100°C (low pressure side)	246	75
	Methanol 2500 psi 100°C (high pressure side)	253	55

Specimens were 0.015" shavings

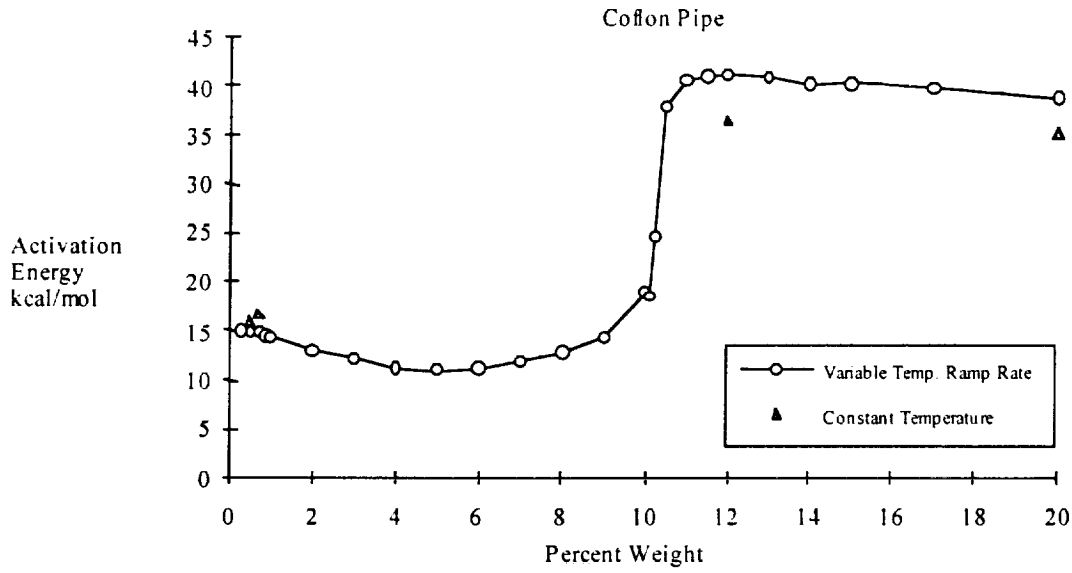

Figure 7-2. Activation Energy Vs. Percent Weight Loss; Comparison Of Variable Heating Rate Experiments And Isothermal Tests; Coflon Pipe.

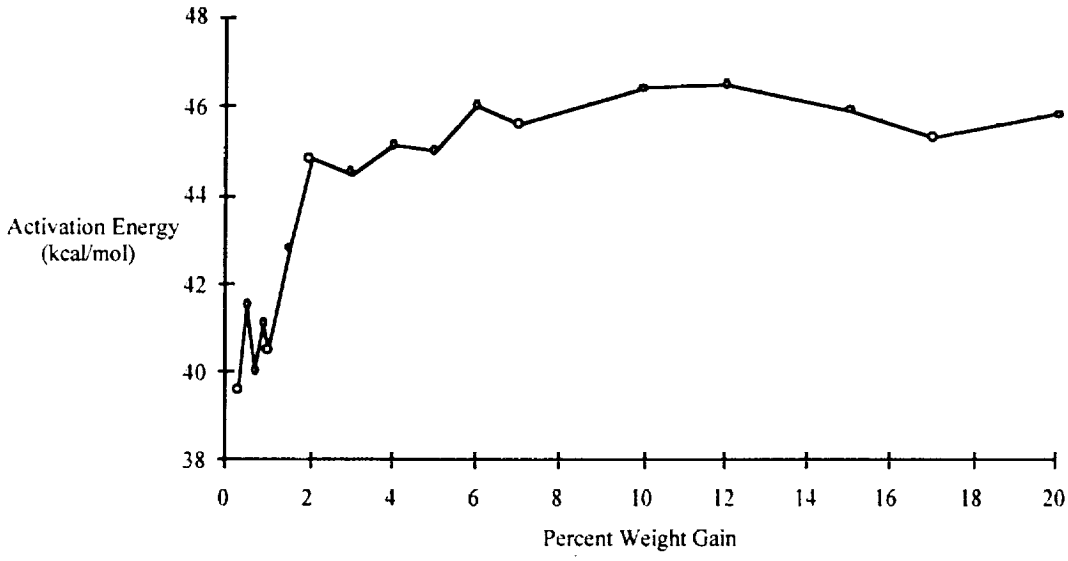

Figure 7-3. Activation Energy Vs. Percent Weight Loss; Activation Energies Were Obtained From Variable Heating Rate Experiments; Tefzel Pipe.

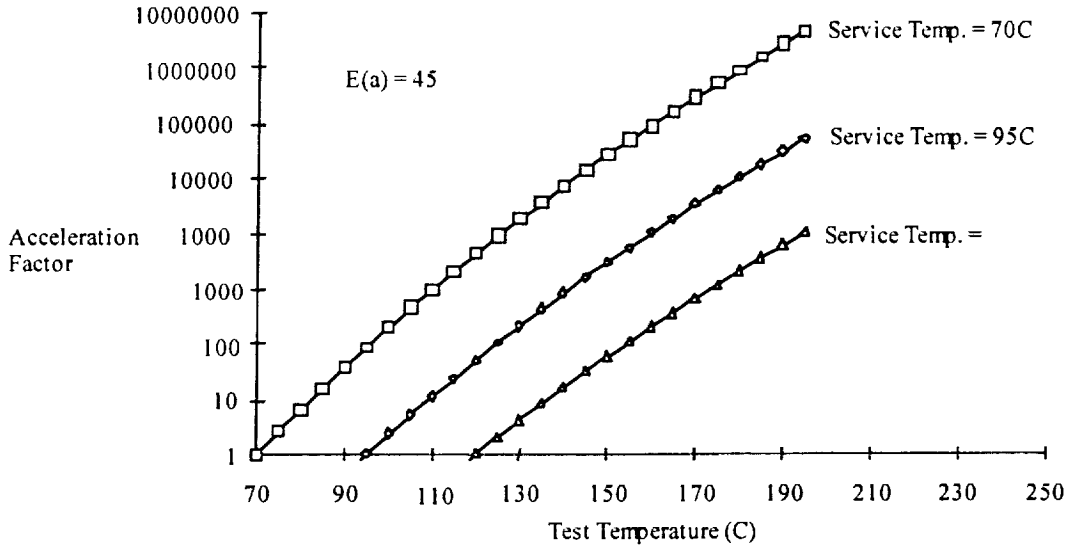

Figure 7-4. Acceleration Factors Vs. Test Temperature At Three Service Temperatures; Activation Energy = 45 Kcal/Mol.

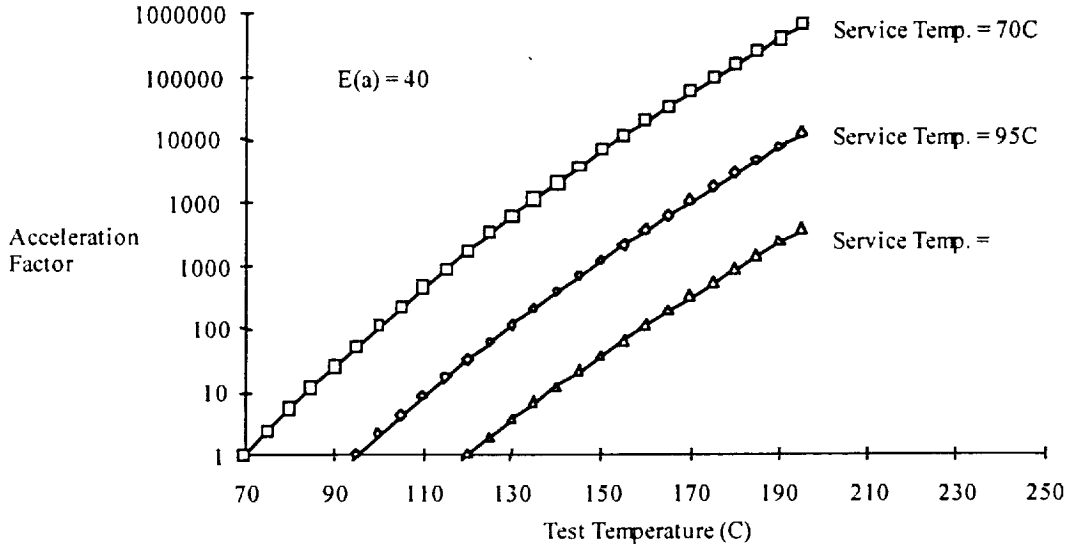

Figure 7-5. Acceleration Factors Vs. Test Temperature At Three Service Temperatures; Activation Energy = 40 Kcal/Mol.

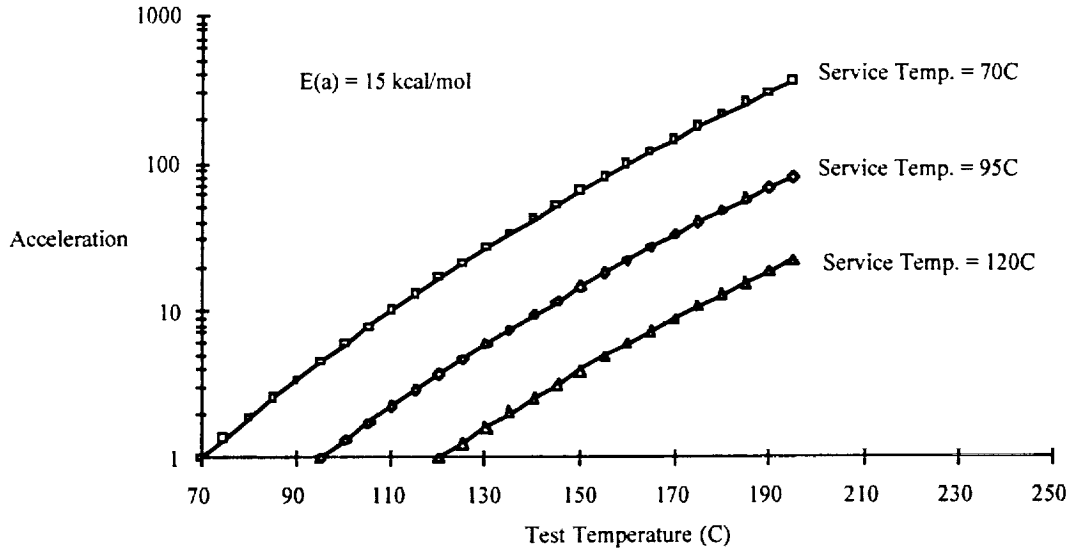

Figure 7-6. Acceleration Factors Vs. Test Temperature At Three Service Temperatures; Activation Energy = 15 Kcal/Mol.

Coflon TGA Results

Virgin and aged specimens were prepared and tested. As shown in Table 7-5 the aged specimens were exposed to 5% H_2S for 7 days at 1000 psi at either 100, 120 or 140°C. The first weight loss onset temperature was significantly higher for the unaged specimen while the second onset temperature remains relatively unchanged comparing the aged with unaged specimens. One possible reason for this behavior might be the loss of low molecular weight fractions produced by the aging process being eliminated at a lower temperature.

It also appears that the specimens that were exposed to high pressure permeation tests contain a smaller amount of the material evolving at the lower decomposition temperature (approximately 3% compared to 8% for the non-permeation specimens).

The highest secondary onset temperature was observed with the specimen that was exposed to high pressure H_2S as a permeant (10% H_2S at 130°C 2500 psi 1 day and 5000 psi 1 day). This may be a result of bulk penetration of H_2S into the specimen causing sulphide crosslinking.

Another feature illustrated in Table 7-5 is the difference in char for the sample tested with methane as a permeant. The other three specimens produced char yields between 18 and 23 percent compared to 2.9% for the methane exposed specimen. An additional specimen was analyzed to confirm this result with similar results.

Table 7-5. Thermogravimetric Analysis Results for Coflon

Aging Temperature[1] (°C)	Permeation Conditions	1st Weight Loss Onset	2nd Weight Loss Onset	Char Remaining
Unaged	None	267°C (8.1%)	482°C (69%)	22.3%
100	10% H_2S 130°C 2500 psi 1 day 5000 psi 1 day	225°C (2.7%)	497°C (79%)	18.1
120	methane 130°C 2500 psi 1 day	170°C (3.2%)	478°C (94%)	2.9
140	None	176°C (7.2%)	488°C (70%)	22.9

1 = Aged samples were exposed to 5% H_2S for 7 days at 1000 psi. Specimens were 0.015" shavings from exposed high pressure surface

Compositional Profile of Aged Coflon Permeation Specimens

In order to determine how high pressure permeation affects the composition of Coflon pipe, thermogravimetric analysis (TGA) was performed. This analysis provides information regarding how plasticizer and other volatile materials migrate through the pipe wall. High pressure permeation testing was performed at MERL using 8 mm thick sections cut from Coflon pipe. After permeation testing the specimens were sent to TRI for analysis. An example of this behavior is shown in Table 7-6. Shown here are the results obtained from the high and low pressure side of a test specimen that was exposed to Fluid F for 4 weeks at 120°C and 5 ksi. Note that the high pressure side contains less residual volatile material than the low pressure side.

Table 7-6. TGA Test Result For Aged Coflon Samples.

Sample	Exposure	Residual Volatiles Including Plasticizer (%)	Weight Retention at 500 °C (%)
T-51 HP Side	Fluid F 120°C 5 ksi 4 weeks	8	37
T-51 LP Side	Fluid F 120°C 5 ksi 4 weeks	12	N/A
T-74	Fluid F 120°C 5 ksi 2 weeks	7	35
T-75	Fluid F 140°C 5 ksi 3 days	8	36
T-76	Fluid F 140°C 5 ksi 5 days	9	36
T-77	Fluid F 140°C 5 ksi 8 days	8	37

TGA of Long-Term Coflon Methane Permeation Test Specimen

Thermogravimetric analysis was performed on a Coflon specimen, T98 (MERL C22), after long term methane permeation testing at 140°C and 5000 psi. This specimen was not exposed to any fluid so that all residual volatile material within the sample should be plasticizer. Sections one mm in thickness were cut from the surface of the high and low pressure sides of the specimen. These were then placed in the TGA sample compartment where a nitrogen atmosphere was maintained while ramping the temperature 10°C per minute.

The results of the TGA indicated that the high pressure side had a residual plasticizer content of 1.9 percent. In comparison, the low pressure side had a plasticizer content of 0.95 percent. This may be due to some molecular "packing" phenomenon occurring on the high pressure side.

Figure 7-7 shows the cross sectional profile of the specimen. Eight 1 mm thick sections were cut from the specimen. These sections were cut from the surface of the high and low pressure sides of the specimen. These were then placed in the TGA sample compartment where a nitrogen atmosphere was maintained while ramping the temperature 10°C per minute. This allows the determination of a residual plasticizer profile through the wall thickness of the Coflon pipe permeation specimen. The onset temperature observed indicates that the residue coming off is primarily plasticizer and not methanol.

Figure 7-7. Cross Sectional Profile Of Methanol/Methane Permeation Specimen, 140 °C And 5ksi

As shown in Figure 7-8, the highest residual plasticizer content was again found on the high pressure side. A transition point appears to occur midway through the specimen For comparison a similar crossectioning for determination of plasticizer concentration profile was performed on unaged Coflon pipe. The results of this test indicated that the plasticizer concentration is very consistent through the wall thickness of the unaged pipe. Differential Scanning Calorimetry (DSC) tests were also performed at the same wall depth locations. The DSC and TGA test results are summarized in Table 7-7.

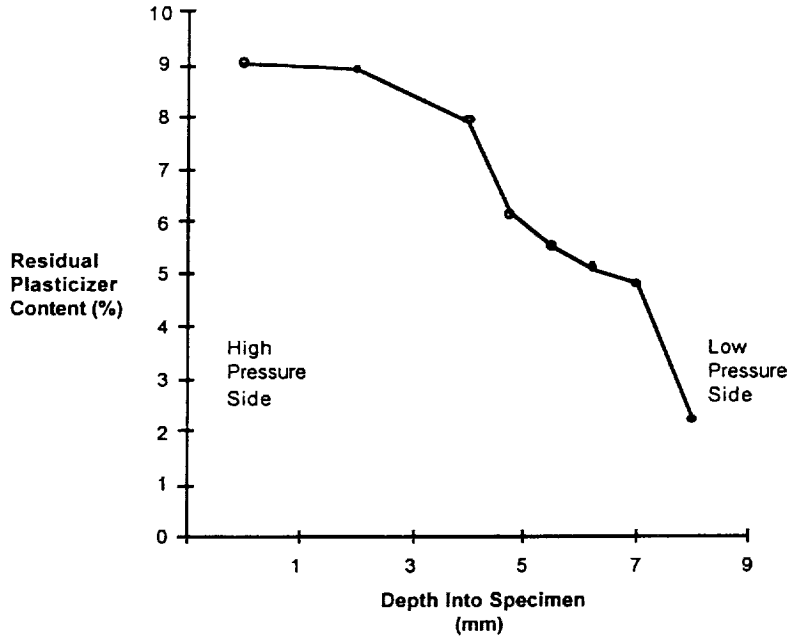

Figure 7-8. Residual Plasticizer Content In A High Pressure Permeation Specimen T99. (MERL C28) CH_4 Permeation Through Methanol 5000 Psi Gas 140°C

Table 7-7. DSC and TGA test results from unaged Coflon Pipe

	Melt Onset (°C)	Melt Peak (°C)	Heat of Fusion (J/g)	Residual Plasticizer (%)	Crystallinity (%)*
1 mm From I.D.	161	170	49.8	11.98	18
Interior of Pipe Wall	163	170	55.2	10.98	11
1 mm From OD	159	168	67.1	10.36	37
Average	161	169	57	11	22

* performed using X-Ray Diffraction

As would be expected, the heat of fusion and crystallinity appear to correlate. The highest crystallinity and heat of fusion were found on the O.D. of the pipe. The plasticizer concentration is relatively constant through the thickness of the unaged pipe but there does seem to be a trend toward higher concentrations near the I.D.

Tefzel TGA Results

The Tefzel specimens as tested consisted of the following:

- Unaged;
- Methanol permeation specimen exposed for 2 days at 100°C and 2500 psi;
- Methanol absorption specimen exposed for 3 days at 150°C and 15 Bar.

One thermal degradation event occurred with all of the Tefzel specimens tested. The onset temperatures for this event for the three cases were very similar, with the range being 516 to 523°C.

Determination of Activation Energies for Coflon and Tefzel Pipe by TGA

Thermal decomposition activation energies were determined using two methods with good correlation observed between the two techniques.

Method 1 - Variable Temperature Rate Tests

This thermogravimetric technique involves heating separate specimens at differing temperature ramp rates while monitoring weight loss. From the thermal curves, the time required to reach a certain weight loss value is obtained. The activation energy is then determined using the method of Flynn and Wall by plotting logarithm of heating rate versus the reciprocal of temperature of constant decomposition level.

$$E = \frac{-R}{b}\left[\frac{d\log\beta}{d(1/T)}\right] \qquad (1)$$

Where:

E = Activation Energy (J/mol)
R = Gas Constant (1.98 cal/mol)
T = Temperature at Constant Conversion (°K)
β = Heating Rate (°C/min.)
b = Constant (= 0.457)

The value of the derivative term (d log β/ [d(1/T)]) is the slope of the line in the Arrhenius plots. The activation energy is then used to determine acceleration factors under conditions of elevated temperature exposure.

Method 2 - Constant Temperature Tests

This is also a thermogravimetric method that involves heating a sample to a predetermined temperature and then recording the amount of time required to achieve a certain level of weight loss. Several different temperatures are used to construct an Arrhenius plot with log time to a certain percentage weight loss versus the reciprocal of the corresponding temperature.

The acceleration factor can then be calculated using the following equation:

$$A = \exp\left[\frac{a}{r}\left(\frac{1}{T_s} - \frac{1}{T_L}\right)\right] \qquad (2)$$

Where:

A	=	Acceleration Factor
a	=	activation energy (kcal/mol)
r	=	Boltzsmann's Constant,
T_S	=	Service Temperature (°K)
T_L	=	laboratory temperature (°K).

The time necessary to achieve a certain percentage weight loss is plotted versus the independent variable, temperature.

Coflon was tested by both techniques, while the Tefzel was tested by the variable heating rate technique alone. Activation energy vs. percent weight loss is displayed in Figure 7-2. Note that the comparison between variable heating rate experiments and isothermal tests show a good correlation between the two methods. The activation energy has a relatively low value, ≅15 kcal/mol, while the plastisizer is being evolved. When most of the plastisizer is removed (≅ 11% by weight for Coflon the activation energy moves to a higher level, ≅40 kcal/mol.

Figure 7-3 shows a similar plot of activation energy vs. percent weight loss for Tefzel pipe material. Here the activation energy begins at 40 kcal/mol during the early weight loss process and stabilizes at 45 kcal/mol at the higher percentage weight losses.

Figures 7-4 through 7-6 show the acceleration factors associated with the three activation energy's values described above. As expected the biggest difference seen when comparing these plots is the low acceleration factors associated with the evolution of plasticizer from Coflon This is a result of the fact that the diffusion process is a relatively rapid process by itself and, therefore, temperature does accelerate the process appreciably.

Thermomechanical Analysis

Yielded Tefzel Specimens

Investigation of yielded gauge-length portions of TEFZEL specimens was performed. Specimens were taken to -150°C after which the temperature was ramped to 200°C.

Table 7-8 summarizes the results. These specimens, having been stressed beyond the yield point, contain extreme residual stresses as evidenced by the data. The specimens were placed in the sample chamber at room temperature followed by lowering of the temperature to -150°C. All of the specimens tested thus far have expanded during the cooling cycle (observed but not plotted). During the ramp to 200°C shrinkage in the axial direction amounts to about 30% while width and thickness increase by about 25%.

Table 7-8. Thermal Expansion Properties of TEFZEL 280

Condition	Time in Methanol min.	Δ Length (%)	Δ Width (%)	Δ Thickness (%)	Δ Volume (%)	α_1 -145 To 10°C PPM/°C	α_2 100 To 110°C PPM/°C	α_3 150 To 175°C PPM/°C
NGL CHS=50	0	-33	26	22	0.47	-8	-3812	-2807
NGL CHS=50	27	-29	21	23	0.70	-5	-2760	-2447
NGL CHS=50	54	-30	25	18	0.36	2	-3643	-2683
NGL CHS=50	10000	-8	4.07	5	0.14	-1	-57	-1727
NS	0	2	1	-13	-1.32	85	628	262

NGL = Necked Gauge Length
NS = Not Stressed
CHS = Crosshead Speed (mm/min)

The control (no stress and no methanol exposure) shrinks through the thickness by 13%. This may be due to residual stresses occurring during the extrusion process.

Thermomechanical Analysis of Unaged Tefzel and Coflon Pipe Specimens

TMA was performed on pipe sections of unaged Tefzel and Coflon. The pipe specimens had the following dimensions.

1. Coflon with 5 mm wall thickness and 70 mm I.D.
2. Tefzel pipe 3 mm wall thickness and 35 mm I.D.

Sections were cut from the pipe samples which were then placed in the TMA specimen chamber. The temperature was ramped 20°C/minute up to 100°C where it was held isothermally while monitoring dimensional change in the thickness of the specimen.

Figure 7-9 shows the results for the tests. During the temperature ramping portion of the test, Tefzel expanded up until reaching ~65°C, at which point a small amount of shrinkage occurred. This was followed by significant expansion beginning at ~95°C. After several minutes at 100°C the specimen seems to have stabilized and is equilibrating.

In contrast, Coflon begins to shrink immediately during the temperature ramp and continues to shrink throughout the test run. After ~27,000 minutes (~2.7 weeks), the specimen thickness is still decreasing and it appears that much more time is needed to reach equilibrium.

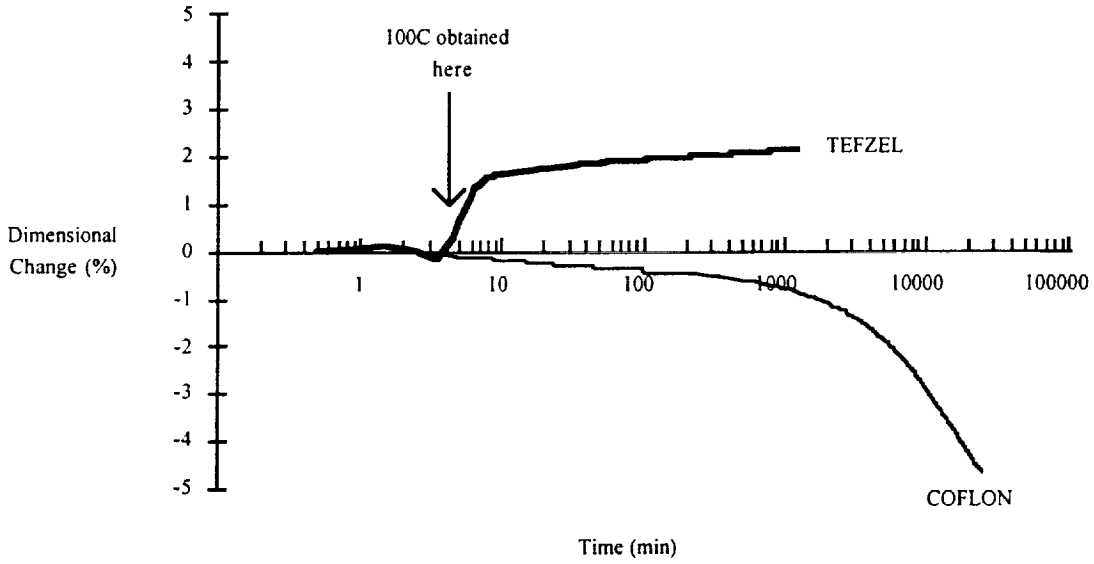

Figure 7-9. Tefzel Pipe-Wall Dimensional Equilibrium At 100°c; Tefzel Pipe Specimen Unaged, 3 Mm Wall Thickness.

The dimensional changes occurring in Tefzel were characterized in all three directions, wall thickness, axial, and circumferential. The equilibrated results are shown in Figure 7-10.

Creep Analysis using TMA

Coflon films cast from PVDF solution were subjected to creep testing in TRI's 943 Thermomechanical Analyzer (TMA) after aging in methanol/EDA. The films were cut into 0.15 inch (3.8 mm) widths. The specimens were then mounted in a tensile fixture. A dead load was applied sufficient to impose a stress of 500 psi. The TMA furnace was then placed around the sample compartment. The sample temperature was ramped up 10°C per minute to 150°C. In this manner the creep behavior was observed while the specimen was undergoing an increase in temperature.

Figure 7-11 displays the results for the unaged Coflon and three of the aged specimens. The specimen which was aged for 17 hours was too brittle to fixture and is not indicated in Figure 7-11 for this reason. A significant increase in the resistance to creep with temperature was noted in the aged specimens. This behavior may be a result of dehydrofluorination and possible subsequent crosslinking within the polymer.

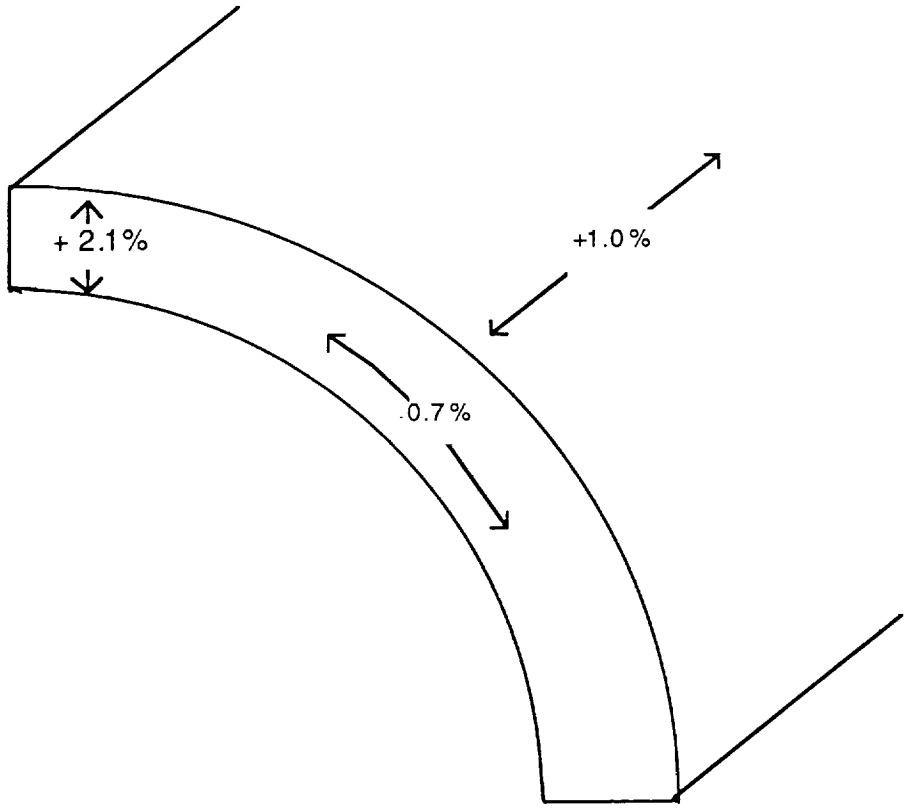

Figure 7-10. Pipe Wall Dimensional Change At 100°C Isothermal For Tefzel

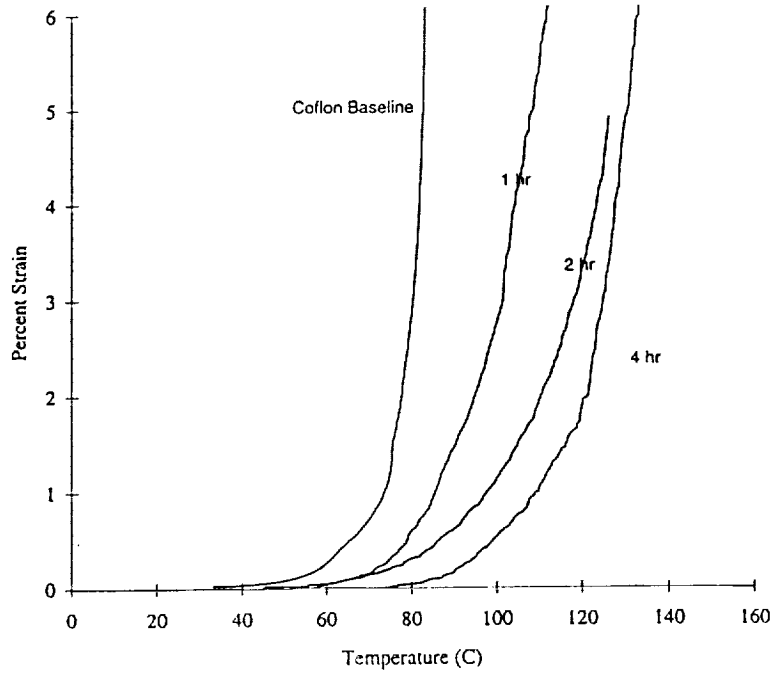

Figure 7-11. Thermal Creep Behavior of Coflon Films Aged in Methanol +1% EDA

Dynamic Mechanical Analysis

Dynamic Mechanical Analysis of Coflon Pipe

Coflon and Tefzel specimens were cut from sheet material in order to perform dynamic mechanical analysis (DMA) tests. The DMA tests were performed at a frequency of 1 Hz with a displacement of 0.5 mm. Figure 7-12 compares the temperature dependence of Coflon and Tefzel. Tefzel appears to be slightly more temperature dependent. Interestingly, both materials have approximately the same modulus at 100°C, which is very close to maximum service temperature.

Tefzel and Coflon specimens were placed in methanol at 23°C in order to observe changes in dynamic modulus with time in this fluid. Figure 7-13 shows the results of these experiments. Tefzel showed a slight (approx. 5%) increase in modulus during the course of the test, while Coflon displayed an equal decrease in modulus.

The sample was then removed from methanol and the dynamic mechanical analysis was continued in air for the next twenty two hours. We noticed an increase in the flexural modulus to a higher level than the initial value. The initial flexural modulus value had increased 1.3% at the end of twenty-two hours from the initial value. The increase in the flexural modulus at the end of the test could be due to the leaching of the plasticizer, an increase in crystallinity, or both of these processes.

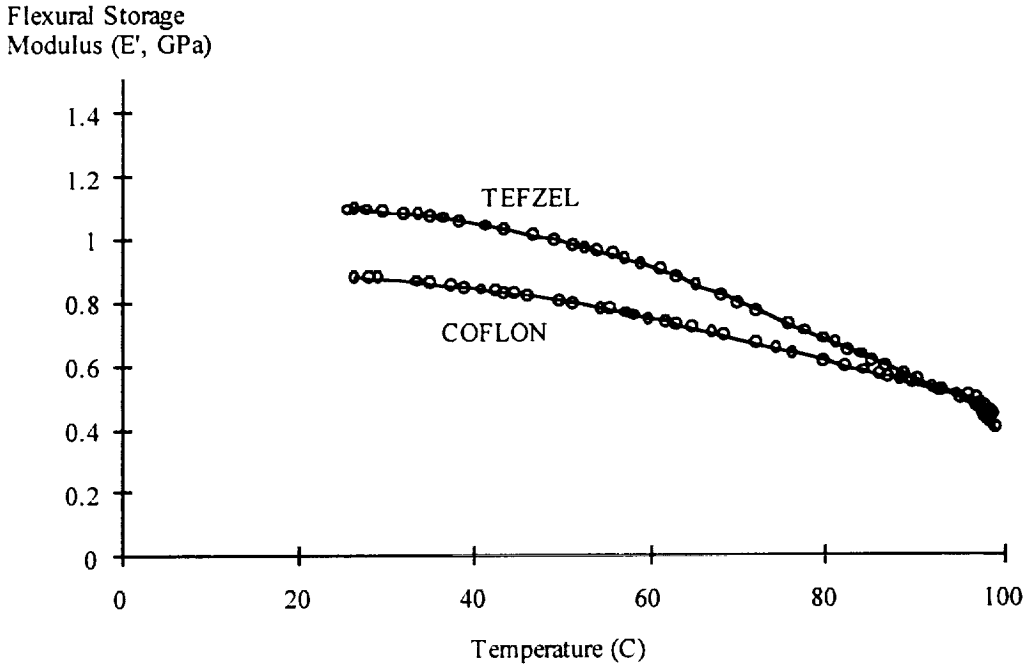

Figure 7-12. Temperature Dependent Modulus of Tefzel and Coflon

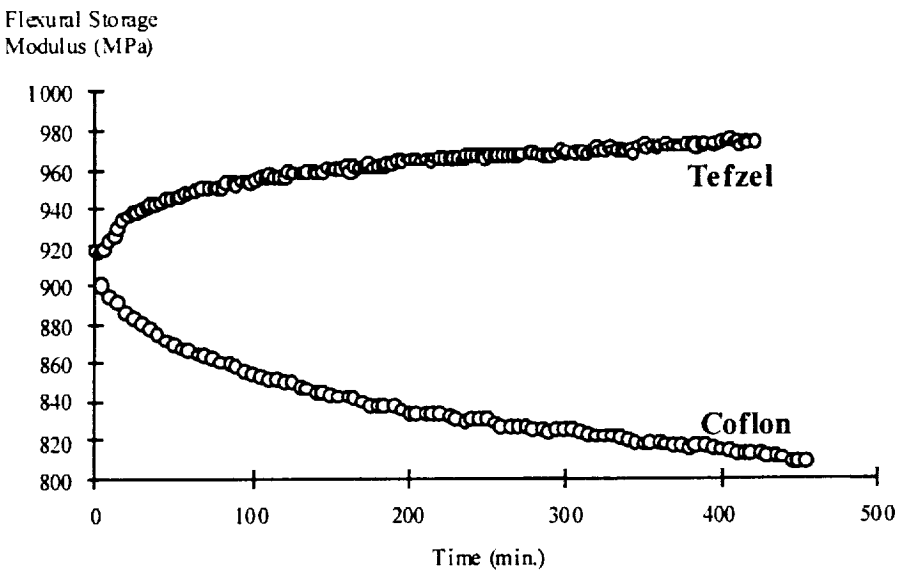

Figure 7-13. Dynamic Mechanical Analysis of Tefzel and Coflon During Methanol Exposure

8.0 Fourier Transform Infrared Spectroscopy

Spectroscopic analyses were performed on Tefzel and Coflon materials before and after aging in order to help identify what chemical changes were occurring during the chemical exposures. In some cases the chemical fluids were analyzed to investigate byproduct chemistries as well. Evidence of dehydroflourination and increases in unsaturation in the PVDF backbone were discovered. No significant changes were observed in the ETFE material (Tefzel).

Hydrogen Sulfide and Methanol Exposures

One of the early evaluations involved the chemical aging of Tefzel in Methanol and Coflon in H_2S at various temperatures and pressures. The Coflon specimens were cut from pipe sections. One of these specimens was tested for methane permeation, and another for H_2S permeation.

The Tefzel specimens were cut from .05 mm. sheet stock material and were exposed to methanol at elevated temperature and pressure. One of these specimens was exposed to methanol permeation for 2 days at 100°C and 2500 psi. An additional specimen was exposed to liquid methanol for 3 days at 150° and, 15 Bar. Virgin specimens of each material were similarly prepared and tested.

Figure 8-1 displays the FTIR results for both the aged and unaged Coflon specimens. For reference purposes a library spectra of PVDF is shown also. The differences seen comparing the library spectra with the unaged Coflon specimen are likely due to the incorporation of stabilizers or residual processing additives in the latter. Another factor that may attribute to the differences is surface degradation of the polymer during processing. Specifically, the absorption band at approximately 1740 cm^{-1} seen in the unaged Coflon specimen is characteristic of carbonyl functionality. After aging in H_2S this peak lessens in intensity dramatically.

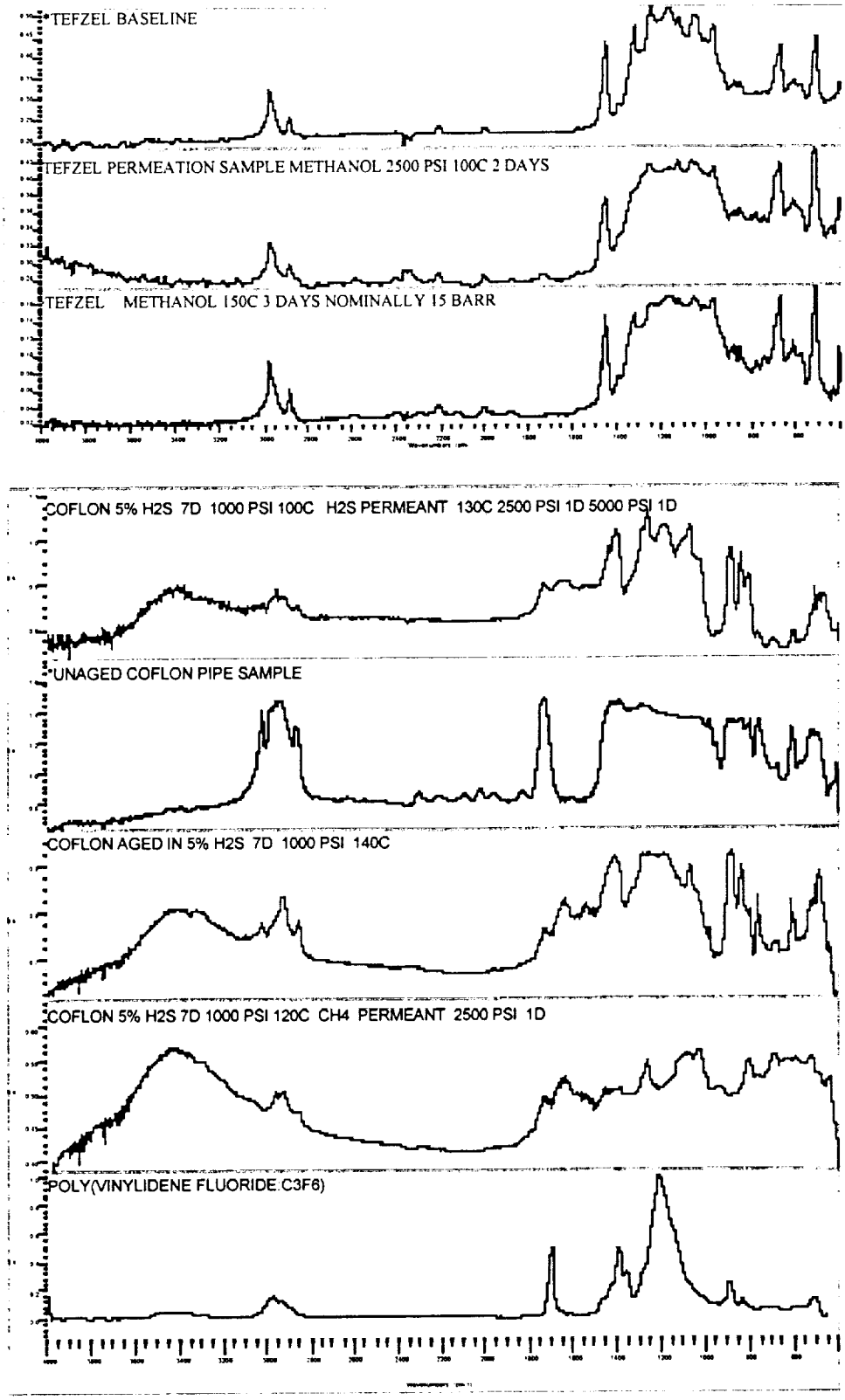

Figure 8-1. FTIR Results After Fluid A and Fluid B Exposures of Coflon and Tefzel

The peak at 1440 cm^{-1} that is associated with C=C and CH_2 functionalities decreases in relative intensity after aging also. The presence of a band at 850 cm^{-1}, after aging in H_2S at 140°C confirms that the changes are due to a decrease in CH_2 and not C=C. Loss of intensity of the CF_2 band at 1200 cm^{-1} after aging is consistent with the loss of HF associated with thermal degradation.

The specimen that was both aged in H_2S and exposed to high pressure methane shows indications of sulphide crosslinking as evidenced by the band visible at 1250 cm^{-1} that is associated with CH_2-S. In addition this specimen has partially lost some C=C character as seen by the decrease in the absorption band at 850 cm^{-1}.

The specimen that was aged in H_2S and exposed to high pressure H_2S shows even more pronounced indications of sulphide crosslinking by the band at 1250 cm^{-1} that is associated with CH_2-S. As shown in Figure 8-1, no significant differences were observed comparing the aged and unaged Tefzel specimens. Specimens resulting from aging in Fluids A-I were similarly tested.

Subsequent to elevated temperature aging of Coflon in Fluids A and B and Tefzel in Fluid A analyses were performed using FTIR. The methanol fluid that was used to age the Coflon at elevated temperature was analyzed using GC/mass spectrocsopy. This analysis identified the plasticizer, dibutyl ester of decanedioic acid, as being the primary compound being leached from the Coflon.

Table 8-1 describes the observations made from the FTIR spectra obtained from the Aged Coflon and Tefzel. These data indicate very little change in chemical composition of either the Coflon or the Tefzel base polymers after aging.

Determination of Degradation and Mechanisms Using Thin Films

Coflon pipe specimens were dissolved in DMAC and films were cast on glass plates. After drying, small (1"X1") film sections were used for aging studies. In a typical experiment, a 100 mL, three neck, round-bottom flask was fitted with reflux condenser and argon inlet. The flask was charged with methanol (50 mL) and ethylenediamine (0.5 mL), and the film was added to this mixture and heated to reflux. After a specified time interval the film was removed, washed with methanol, dried and analyzed by infrared spectroscopy.

Coflon films were aged under several different conditions and the results are summarized in Table 8-1. All of the films were discolored by the aging process, and films subjected to prolonged aging acquired a dark color and became brittle.

The infrared spectra of old Coflon films showed that peaks at 3370, 2149 and 1642 cm-1 appeared after aging. A comparison of the infrared spectra of new PVDF film before and after aging showed that the absorption at 1642 cm-1 moved to 1599 cm-1. This may be due to reaction of the plasticizer.

Table 8-1. FTIR Observations of Aged Specimens

Sample I.D. #	Exposure Conditions	Visual Appearance and Observations	Chemical Analysis and Observations
T-32 Coflon	14 days at 140°C	Solid retrieved by evaporation from fluids after exposure	Broad hydroxy functionality, decreased carbonyl absorption
T-36 Coflon	Residue from evaporated fluid A 140°C vapor pressure exposure with Coflon	Mixture of solids in fluid and retrieved from fluids after exposure, brown waxlike substance	Polyethylene or polypropylene type spectrum, hydrocarbon type
T-31 Coflon	Collection of deposited Coflon 13 days Fluid A exposure 140°C vapor pressure	Spongy residue deposits from bottom of cell: white, porous, extremely physically degraded	Splitting of 1200cm-1 peak, decreased carbonyl absorption
T-29 Tefzel	Tefzel, 6 days fluid A 140°C vapor pressure exposure	White, translucent, good integrity	Few minor changes
T-35 Coflon	Debris collected from pressure cell after 14 days fluid A 140°C vapor pressure test of Coflon	Film from cell walls, light brown like paper	Hydroxy functionality evident, decreased carbonyl
T-30 Coflon	Remains of Coflon 4 point bend	White spongy porous shell of sample fractured during test	Decreased carbonyl absorption
T-26 Coflon	Sample tested at 23°C, after 14 days in fluid B at 140°C 5000psi	White, opaque, with good integrity, ductile	Decreased Carbonyl absorption, new peaks at lower wavenumbers indicating increased hydrocarbon presence
T-32 Coflon	Residue of filtered methanol from 13 days exposure with Coflon sample 140°C vapor pressure	Extremely porous and brittle light brown material	Broad hydroxy absorption, decreased carbonyl absorption
T-34 Coflon	Unstrained Coflon bar fluid A at 140°C, vapor pressure for 14 days	Dark skin to material, good physical integrity	Decreased carbonyl absorption, broad peaks at high wavenumbers

Chemical analysis of aged Coflon films indicated that composition is dependent on aging conditions (Table 8-2). In run 1 (10% EDA, reflux, 24h), the film suffered a drastic reduction in percent fluorine (from 59,38% F in PVDF to 16.19%) accompanied by an increase in C, H, and N percentage. They also became extremely dark (black). Run 3 (1% EDA, reflux, 16h) also resulted in some decomposition (lowered %F and raised values for % C, H and N). However, runs 2 and 4 (much milder conditions) left the PVDF analyses unchanged.

Table 8-2. Chemical analysis of aged PVDF films.

Run No	Aging			IR (cm^{-1})
	Solvent	Temp. (°C)	Time (hr.)	
1	MeOH + 10% EDA	Reflux	24.0	3372(b), 2945(s), 2149(w), 1642(b)
2	MeOH + 1% EDA	Reflux	1.5	3378,(b) 3021(s), 2979(s), 1642(w), 1407(s), 1208(w), 1027(b), 882(s)
3	MeOH + 1% EDA	Reflux	16.0	3384(b), 3021(s), 2979(s), 1601(b), 1453(s), 1410(b), 1264(b), 878(s), 837(s)
4	MeOH + 1% EDA	Room	16.0	3380(b), 3021(s), 2979(s), 1452(s), 1388(b), 1214(b), 1027(b), 886(s), 837(s)

EDA = Ethylene Diamine

UV Spectroscopic Results

A Varian DMS 200 UV/Vis spectrophotometer was used for the ultraviolet measurements. The UV absorption at 290 nm of the PVDF films aged in methanol/EDA were recorded at room temperature. Absorption at this frequency is known to be associated with C=C double bonds. An increase in the absorbance was found after aging of the PVDF films. This growth in absorbance translates into a decrease in percent transmittance in the samples. The absorbance change was found to increase with time of exposure to the methanol/amine mixture. Figure 8-2 shows the UV results as a function of time.

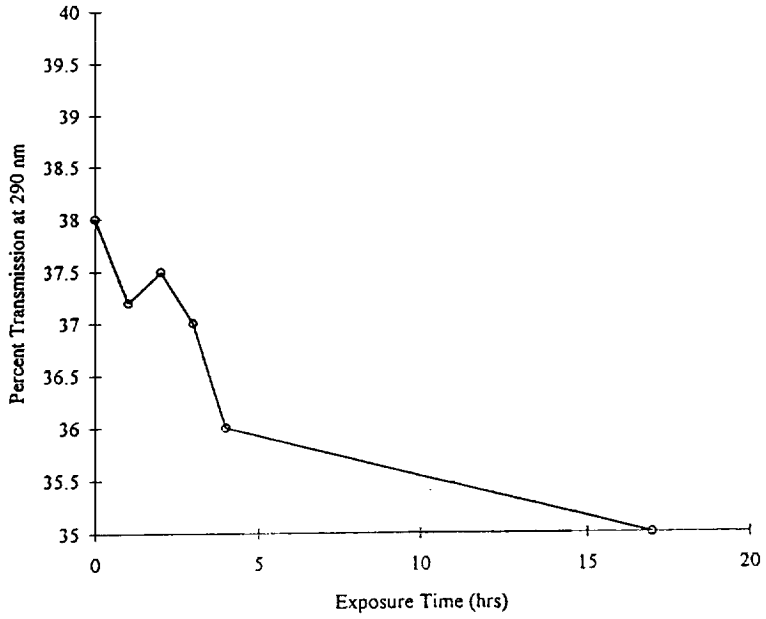

Figure 8-2. Aged Coflon Films Changes in UV Absorption at 290 nm After Exposure to Methanol +1% EDA

9.0 GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

We investigated accelerated high temperature aging of the Coflon material and analyzed the liquid exudate using gas chromatography coupled with mass spectrometry. The database search in many instances provided the best match with a dibutyl ester of decanedioic acid. The search routine can only match those compounds catalogued in the library that contains approximately seven hundred thousand compounds. The tests were conducted on liquids (methanol) after Atlas cell aging.

We conducted GC/Mass Spec on Sample T-89 extracted with methanol. The extract showed primarily the presence of the dibutyl ester of decanedioic acid. Also evident was the free acid decanedioic acid. The decanedioic acid is a degradation product of the plasticizer.

10.0 HIGH PRESSURE AGING

High pressure tests were performed in a modified Fluid G, which we will call G2. In this case the ethylene diamine concentration was increased to 3 percent in methanol. Coflon pipe sections and powdered Coflon were exposed in pressure cells at 1700 psi at three separate test temperatures, 70°C, 110°C, and 130°C. The primary purpose of the pressure tests in Fluid G2 was to further elucidate the aging mechanism of PVDF degradation.

Test Apparatus

Tests were performed in a high pressure Atlas cells which was graciously loaned to TRI for the CAPP project by CONOCO. The configuration for chemical exposure cell is indicated in Figure 10-1. The Atlas cell symmetry axis is horizontal, and the end plates are operated on edge, sealed against the body of the cell with O-rings. For these tests each cell was half filled with the EDA/MeOH liquid and pressurized to 1700 psi with CO_2 gas. Provisions for heating and monitoring the temperature of the liquid are incorporated into the cell. The cell is also plumbed to allow the gas pressure to be monitored and adjusted as necessary. Pressurization of the test chambers was accomplished using a double-piston high pressure intensifier.

Sample Preparations

Two types of samples were prepared for exposure in the Atlas pressure cell. Coflon pipe sections, and powdered Coflon. The following sections describe how the two types were prepared.

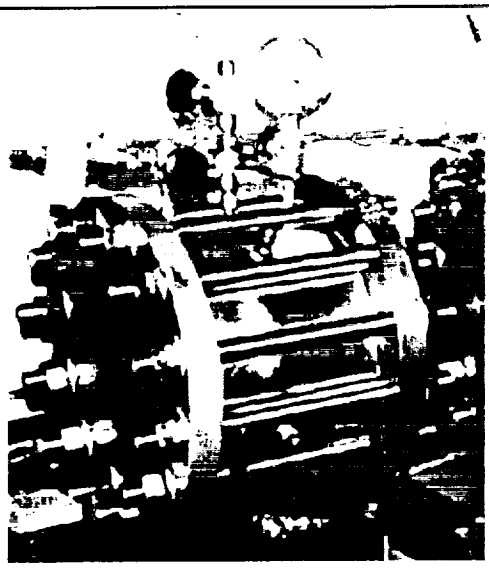

Figure 10-1. Atlas Pressure Test Cell

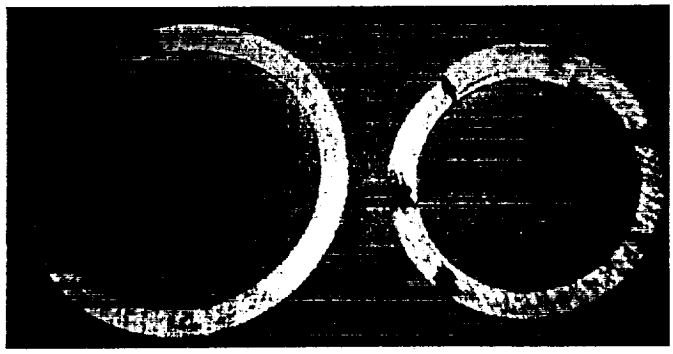

Figure 10-2. Unaged Coflon Pipe Sections. Section On The Right Was Cut Prior To Exposure.

Pipe Sections

Pipe sections were cut in approximately 2 mm lengths. These thin sections were chosen so that maximum deplasticization and diffusion of the ethylenediamine/methanol mixture could occur during the seven day test. Two pipe section specimens each were included in the 110°C and 130°C experiments. One of the two ring specimens was cut perpendicular to the pipe axis in order to allow free contraction. The other specimen was left intact to observe constrained contraction after exposure. Figure 10-2 shows both the cut and un-cut versions before exposure.

Powdered Materials

Powdered Coflon material was also used in order to facilitate deplasticization and diffusion of fluids into the polymer during the pressurized tests. The pipe section rings, described in Section 1.2.1, were cut into smaller sections and placed into a liquid nitrogen freezer mill for ten minutes. This process was repeated until enough powder was collected to perform the aging experiments (~20 g).

Test Conditions

Three temperatures were used in the high pressure Atlas cell tests, 70°C, 110°C, and 130°C. The Atlas cells were partially assembled and the powdered Coflon and Coflon pipe sections were placed inside. The cell was then completely bolted together. The cell was then filled half-way with a mixture of 3% EDA/97% MeOH. After reaching the appropriate temperature, 70°C, 110°C, or 130°C, CO_2 was introduced into the cell and the pressure raised to 1700 psi (117 bar). The cell was insulated with fiberglass and left for seven days. At the end of the seven day exposure the cell was drained and opened. Fluid samples were retained for analyses.

The powdered Coflon was rinsed with methanol and dried in an oven for one hour at 70°C. Figure 10-3 shows the Atlas test cell after 70°C test with Coflon powder.

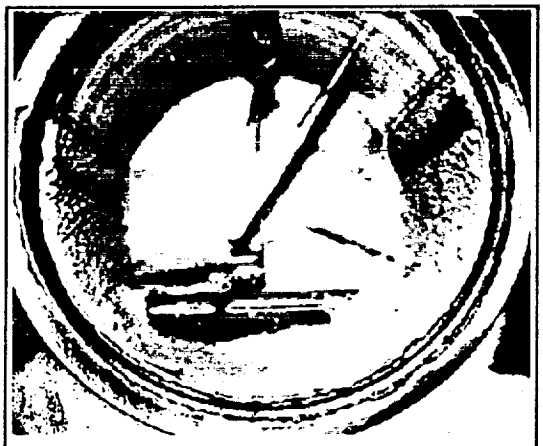

Figure 10-3. Atlas Test Cell After 70 °C Test With Coflon Powder

Chemical Analysis Assessment of Aging Effects

We have conducted a variety of chemical analysis to detect changes in Coflon and Tefzel when aged. We have detected significant changes in molecular weight and percentage crystallinity for the materials. Using infrared spectroscopy we have noted decreases in plasticizer and formation of double bond character in Coflon. We have derived an activation energy in association with the crystallinity change of Coflon.

Coflon Powder Samples

The results on four powder samples, three aged in the Atlas cell, are shown below in Table 10-1.

Table 10-1. Percent Crystallinity Results For Coflon Powder Samples

Sample	% Crystallinity	Exposure
CBP	41%	Laboratory Ambient
CP70	37%	Fluid G2 70°C 1 week
CP110	32%	Fluid G2 110°C 1 week
CP130	18%	Fluid G2 130°C 1 week

The results show a decrease in crystallinity after aging.

The changes in crystallinity were used to construct an Arrhenius relationship as displayed in Figure 10-4. An activation energy of 3 kcal/mole was obtained for the process. This is a rather low activation energy indicating that the energy needed to initiate the degradation reaction is relatively small. Likewise, within the range tested, the effect of temperature on acceleration of the process is also relatively small.

We attempted to model the data considering the decrease in crystallinity to be a first order reaction. The reaction rate was taken to have an Arrhenius temperature dependence. With the data available this led to three equations and three parameters, two of which were known previously. The three equations were solved for the third parameter leading to three fairly different values for the

reference reaction rate. We concluded that the model considered did not constitute an adequate representation of the data. In order to further define the mechanism additional testing at other temperatures will be needed.

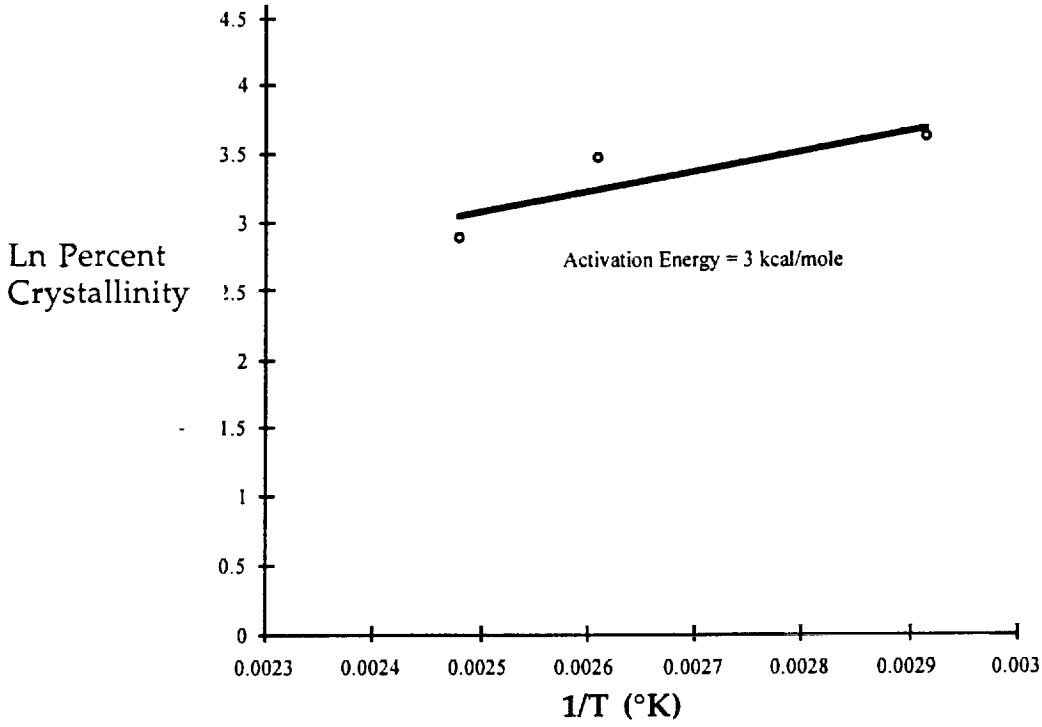

Figure 10-4. Plot Of Arrhenius Relationship Of Aged Coflon Powder

The most interesting result of this analysis was the fact that, in addition to crystallinity changes upon heating, a structural change is also observed upon heating. The raw data composite plot containing the baseline, 70°C, and 110°C Coflon powder in Appendix One, shows the peak shift occurring at the higher 2θ range (lower d-spacing). In Table 10-2 we see the d-spacings in this region increasing upon heating.

Table 10-2. Shifted Peak D-Spacing for Coflon Powder Samples

Sample		D-Spacing for Shifted Peak	Δd
CBP		2.19A	
CP70		2.20A	+0.01 A
CP110		2.25A	+0.05A
CP130		Peak Not Significant	+0.05A

Again, we are seeing structural changes as well as crystallinity changes over this cross section. The pattern taken at the extreme outer wall of the tube shows a

completely different and more ordered structure, as seen by the crystalline peaks emerging between 35°C and 60°C 2θ. This increased order could be due to differences in the fluorine dipole moments and atomic arrangement as discussed in the section above. The amorphous scattering is also increasing as shown by the increasing background intensity.

This experiment represents a classic skin-core X-Ray diffraction result. It does suggest that the structural change is due to a difference in the cooling rate between the two walls.

Analyses of Aged Coflon Powder.

Several aspects of the aged powdered Coflon material were analyzed. First, the residual volatile content, including plasticizer, is shown in Table 10-3. The volatile content decreased upon aging at 70°C and 110°C. However, at 130°C the residual content increases significantly. This may be due to the presence of low molecular weigh products of the degradation reaction. In addition, we see from the DSC results, also in Table 10-3, that the number of components appearing after aging is increasing with exposure temperature.

Table 10-3. Aged Powdered Coflon Pipe Results

Sample	Exposure	Residual Volatiles Including Plasticizer (%)	Weight Retention at 500 °C (%)	Weight Retention at 600 °C (%)	Melt Onset °C	Melt Peak °C	Heat of Fusion (J/g)
Baseline Coflon Powder	None	10.97	41	30	144	168	51
CP70	EDA/Methanol 7d at 70°C	3.52	52	34	162	172	77
CP110	EDA/Methanol 7d at 110°C	1.86	44	33	159 175	171 171	56
CP130	EDA/Methanol 7d at 130°C	9.13	55	50	51 165	86 171	224 7.3

Another outstanding feature is the weight retention at 500°C which remains fairly constant at around 33% except for the 130°C exposure where an increases to 50% was observed. This appears to be a verification that some degree of crosslinking is occurring resulting in a more stable char.

Analyses of Aged Coflon Pipe Sections

Again with the 130°C aged Coflon pipe sections the weight retention at 600°C is greater than observed at the lower exposure temperatures. As shown in Table 10-4 we also detected, as with the powder, an increase in the number of endothermic events in the DSC data indicating conversion to a multi-component material.

Table 10-4. Aged Coflon Pipe Section Results

Sample	Exposure	Residual Volatiles Including Plasticizer (%)	Weight Retention at 500 °C (%)	Weight Retention at 600 °C (%)	Melt Onset °C	Melt Peak °C	Heat of Fusion (J/g)
Baseline	None	11	41	33	159	170	49 - 67
PS110	7d 110C 3% EDA/Methanol	3	53	35	161 169	166 172	100
PS130	7d 130C 3% EDA/Methanol	7	48	44	88 192 212	134 195 217	318 2.5 2.7

Residual Strain Before and After Aging Coflon Pipe Sections

Additional pipe sections were cut and placed into the high pressure test chambers along with the powdered Coflon for the 110°C and 130°C tests. Three sections were placed in the pressure cell during each experiment. Additional specimens were exposed to 110°C at atmospheric pressure with no fluid for comparison. After the one week aging cycles the sections were removed from the test cells and measured to determine shrinkage effects caused by exposure to the high temperature and pressure in the EDA/methanol mixture. Dimensional changes were primarily obtained for the 110°C test. Sufficient pipe section material was not available for the 70°C test. Pipe sections were placed in the 130°C test but were deformed and degraded so severely that only a few measurements were possible.

Residual Strain in Pre-Cut Pipe Sections

Two of the three specimens that were placed in the cells were cut perpendicular to the axis of the pipe prior to the test to allow for free contraction of the specimen. Immediately after cutting, the specimens contracted circumferentially approximately three percent corresponding to a residual hoop stress of 4500 psi. This residual stress is primarily due to thermal drawing history of the pipe during the extrusion process. Knowing the residual hoop stress we can calculate the internal pipe pressure needed to compensate for the residual stress by:

$$q = \frac{qt}{r}$$

where:

r = radius
t = wall thickness
q = internal pressure

After exposure, the additional contraction of the cut sections was measured and found to have a total circumferential shrinkage of 17 percent for the specimens exposed to the EDA/methanol fluid at 110°C. Similarly an identical pre-cut specimen that was simply deplasticized for one week at 110°C had a circumferential shrinkage of 15 percent. It was also interesting to note that this specimen shrank 9.2% during the first ten minutes of the oven exposure indicating that most of the dimensional change is a result of thermal processing history. One dimension was measured for the specimen that was exposed to the EDA/methanol fluid at 130°C. The wall thickness was found to shrink by 7.2% after the seven day exposure. This was significantly higher than any of the other specimens tested. Table 10-5 summarizes the dimensional changes occurring in the various pipe sections tested.

Table 10-5. Dimensional Changes in Coflon Pipe Sections

	Wall Shrinkage (%)	Length Shrinkage (%)	Initial Circumferential Shrinkage Prior To Exposure (%)	Circumferential Shrinkage After Aging (%)	Weight Loss (%)
Aged 7d 110°C 3% EDA/Methanol; Pre-Cut	2.45	6.55	3.00	17.00	3.40
Deplasticized 7d 110 Pre-Cut	1.70	< 1%	3.00	15.00	4.80
Aged 7d 130°C 3% EDA/Methanol	7.20	N/A	N/A	N/A	N/A
	Wall Shrinkage (%)	Length Shrinkage (%)	Circumferential Shrinkage After Aging (%)	Circumferential Shrinkage After Aging The Specimen Then Cutting (%)	Weight Loss (%)
Aged 7d 110°C 3% EDA/Methanol; Cut After Exposure	2.51	4.44	1.48	2.59	2.80
Deplasticized 7d 110°C Cut After Exposure	1.88	< 1%	2.60	10.70	4.57

Residual Strains in Pipe Sections Cut After Exposures

The Coflon pipe specimens that were not cut perpendicular to the axis of the pipe were exposed to either an elevated temperature fluid or air atmosphere as described in Table 10-5. These specimens were intact and not as free to contract compared to the pre-cut specimens. Because of this constraint, we observed a significant decrease in the amount of circumferential shrinkage after aging (~1-3%). After making the dimensional measurements subsequent to aging, the specimens were then cut and measured. In this case the fluid exposed specimen had a much smaller residual strain compared to the specimens conditioned in air at 110°C, (2.6% vs. 10.7% respectively). Figure 10-5 shows the severe cracking observed in the 130°C aged Coflon pipe sections.

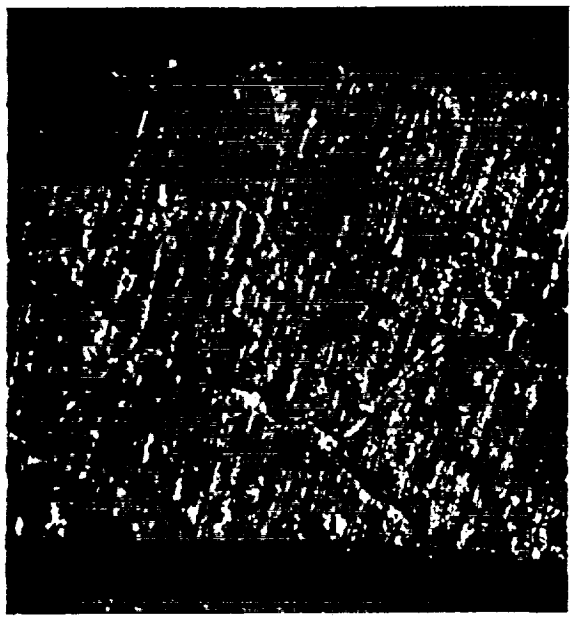

Figure 10-5. Cross Section of 130°C Aged Coflon Pipe Section

11.0 RAPID LOADING AND STRESS RELAXATION OF PIPE SECTIONS

Specimens were cut from virgin Coflon and Tefzel pipe sections. The specimens were cut in 0.5" (12 mm) widths from pipe with the following dimensions.

Tefzel Pipe Sections:	Coflon Pipe Sections:
ID = 3" (76 mm)	ID = 3" (76 mm)
OD = 3.2" (82 mm)	OD = 3.5" (89 mm)
Wall = 0.13" (3.4 mm)	Wall = 0.28" (7 mm)

Specimens were expose to methanol for two weeks at 65°C. Testing was accomplished by fixturing specimens in a split ring fixture situated within a temperature controlled chamber in a Model 4505 Instron. Appropriate loads were applied at a rate of two inches per minute. The stress imposed on the specimens was calculated by assuming a differential internal pipe pressure of 200 psi. From this value the circumferential hoop stress was calculated, and finally the load needed to simulate the service stress was derived. Three test temperatures were used, 50°C, 75°C, and 100°C. The loading portion of the tests were analyzed in order to ascertain any effects on rapid loading modulus resulting from methanol exposure.

Coflon Rapid Loading Results

As seen in Figures 11-1 and 11-2 the rapid loading response of the baseline and methanol aged specimens were different. Before methanol exposure, the Coflon specimens appear to be more temperature dependent at lower strains. This may be occurring as a result of the plasticizer being leached from the polymer by methanol. The moduli of the methanol exposed Coflon tested at 100°C appears to have decreased as a result of methanol exposure.

Tefzel Rapid Loading Results

Figures 11-3 and 11-4 show the results for Tefzel in the baseline condition and after methanol exposure. In this case the moduli of the methanol exposed specimens is affected primarily at the 100°C test temperature where a significant lowering of modulus is observed compared to the baseline data.

Stress Relaxation

Stress relaxation behavior of Coflon and Tefzel pipe sections were determined in a split-ring tension test emulating 200 psi differential internal service pressure. The testing was conducted at three temperatures in order to determine the activation energy for the process. An activation energy was determined for the process of 3 Kcal/mol. Activation energies below 5 Kcal/mol indicate that no primary bond breaking is occurring.

Coflon Stress Relaxation

Baseline Coflon stress relaxation data are presented in Figure 11-5. The baseline data obtained at the 50°C and 75°C test temperatures behave in a fairly conventional manner. At the 100°C test temperature and after an extended time period, the plateau seems to converge with the data obtained at 50°C and 75°C. This behavior is probably due to plasticizer diffusing from the polymer resulting in shrinkage of the specimen which in turn causes the load to decrease a slower rate.

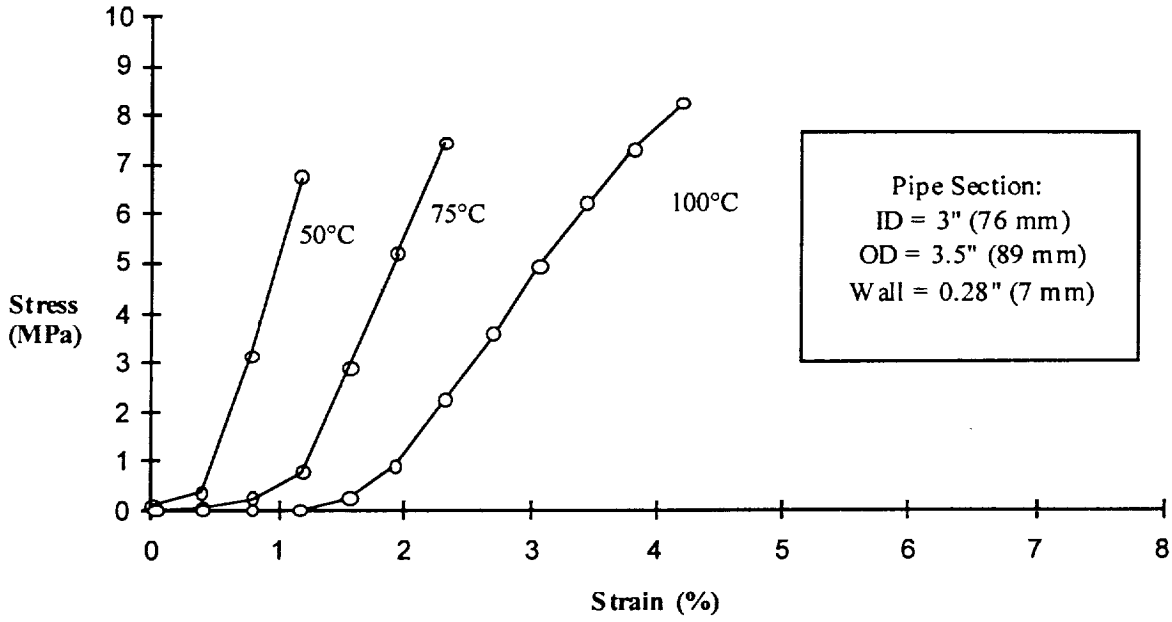

Figure 11-1. Coflon Pipe Section Rapid Loading; No Chemical Exposure

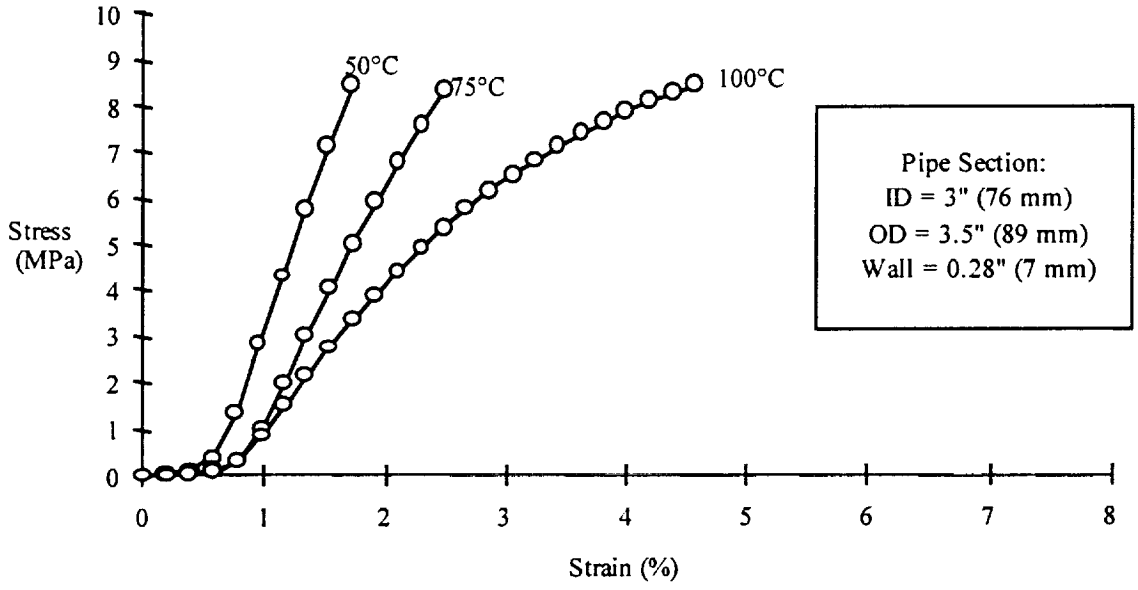

Figure 11-2. Coflon Pipe Section Rapid Loading After Two Weeks in Methanol at 65°C

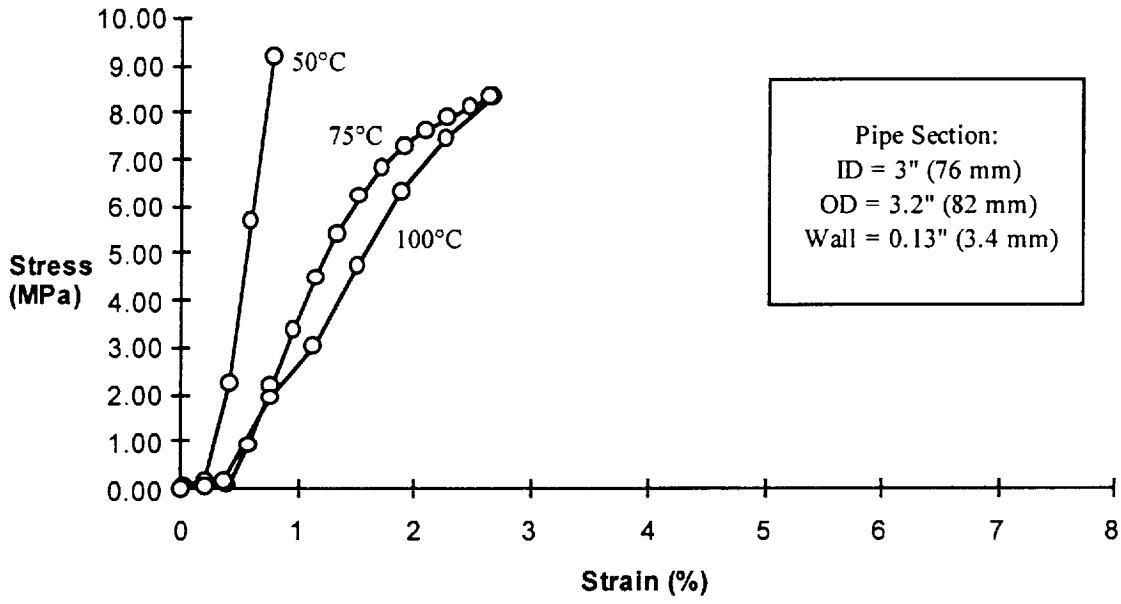

Figure 11-3. Tefzel Rapid Loading Baseline. No Chemical Exposure

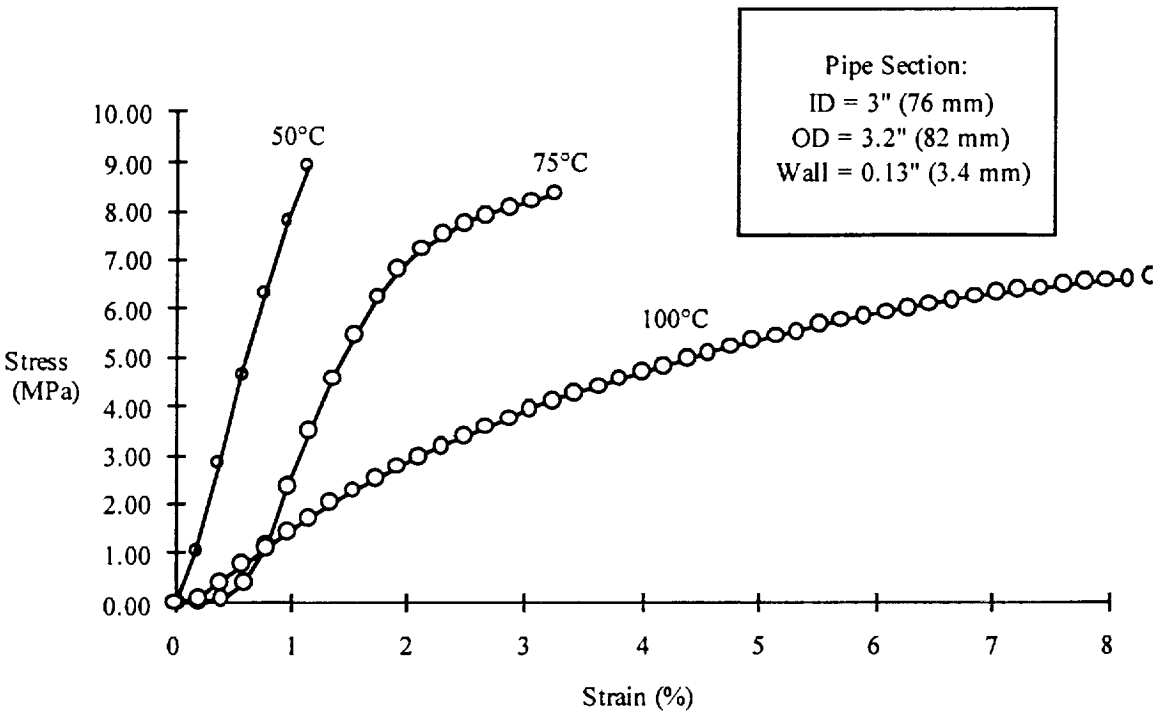

Figure 11-4. Tefzel Rapid Loading After Two Weeks in Methanol at 65°C

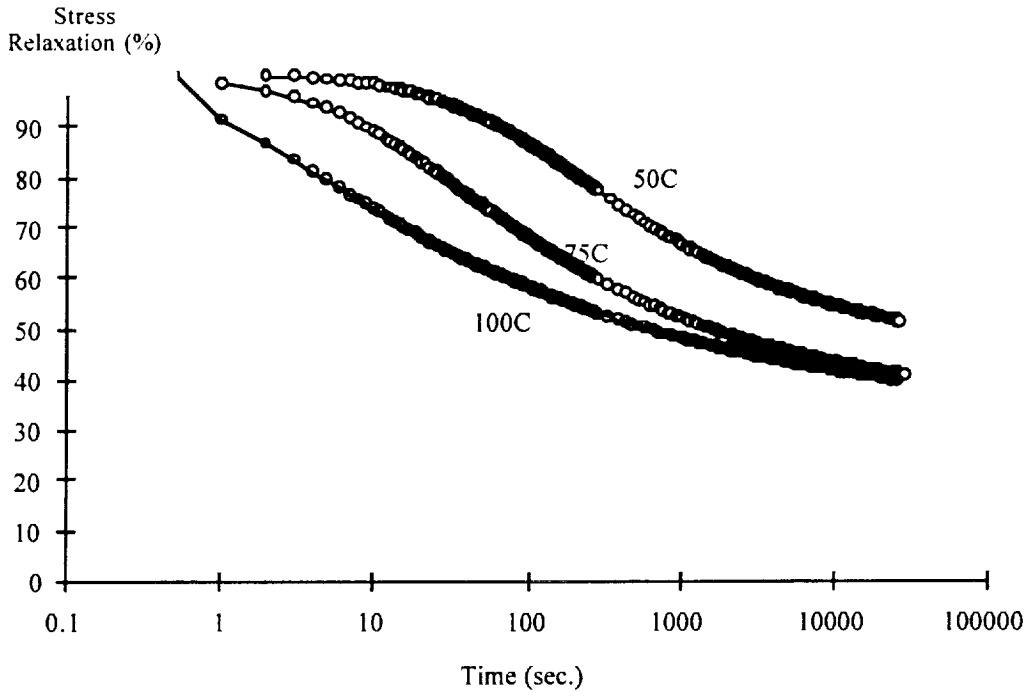

Figure 11-5. Coflon Baseline Stress Relaxation

The methanol exposed Coflon presented in Figure 11-6 also exhibits the change in relaxation rate because of diffusion of both plasticizer and absorbed methanol from the polymer. At 50°C, and more so at 75° and 100°C, the rate of stress decay not only decreases but reverses because of dimensional shrinkage occurring in the pipe section.

Tefzel Stress Relaxation

The baseline results obtained from Tefzel at 50°C and 75°C were very similar to those performed on the methanol exposed specimens at the same temperatures. Figures 11-7 and 11-8 indicate the stress relaxation profile. In contrast, the results for the Stress relaxation performed at 100°C on the methanol exposed specimen showed a smaller overall relaxation than seen previously. This occurred because of the high degree of strain induced to obtain the desired load.

Weight Change of Coflon and Tefzel

All of the specimens that were exposed to methanol were evaluated for weight changes occurring during the two week period. On average, the Coflon specimens showed a decrease in weight of 1.06%. This decrease is possibly due to the displacement of plasticizer by methanol.

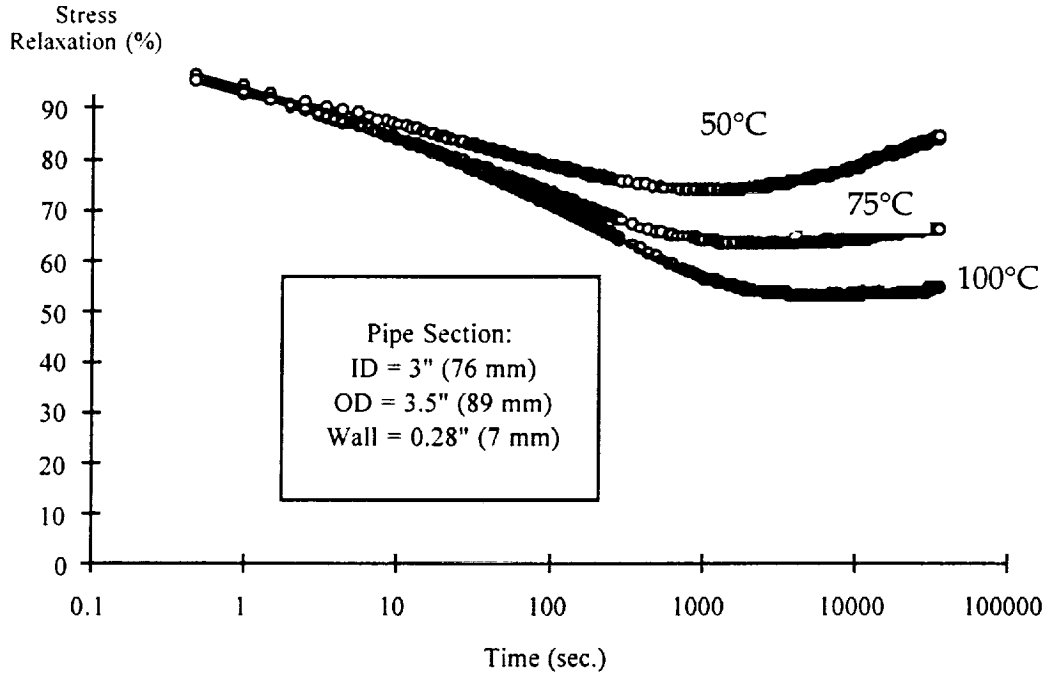

Figure 11-6. Coflon Stress Relaxation After Two Weeks in Methanol at 65°C

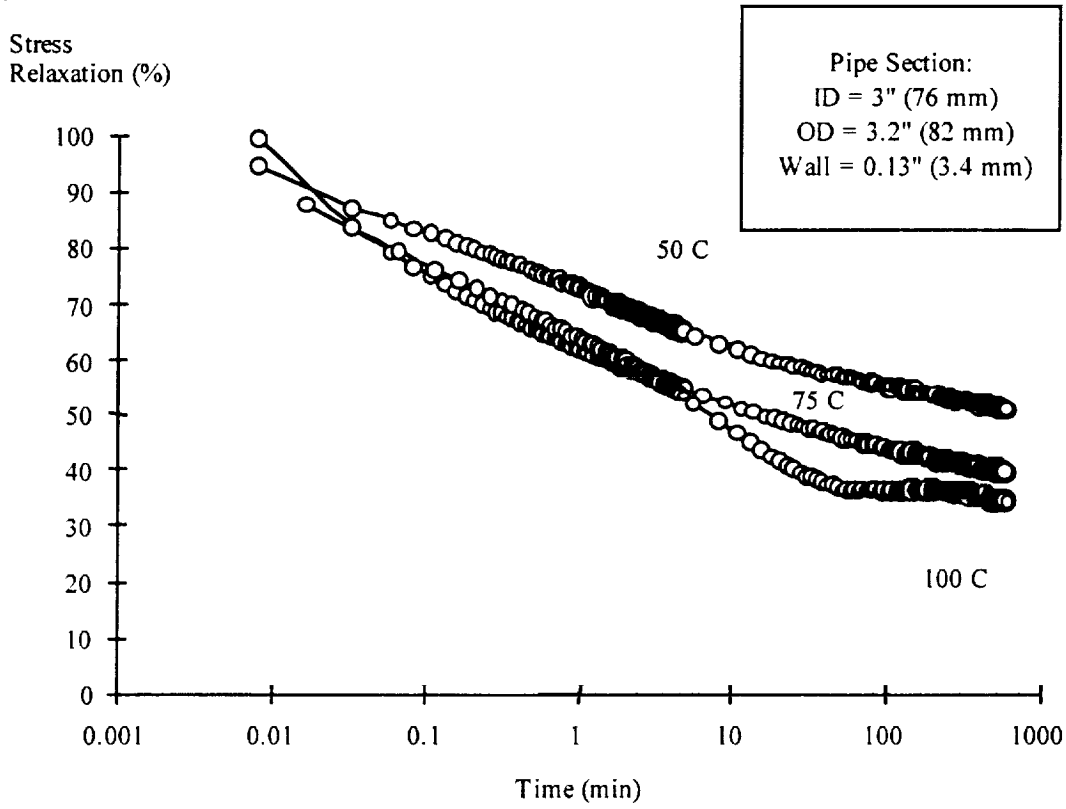

Figure 11-7. Baseline Tetzel Relaxation

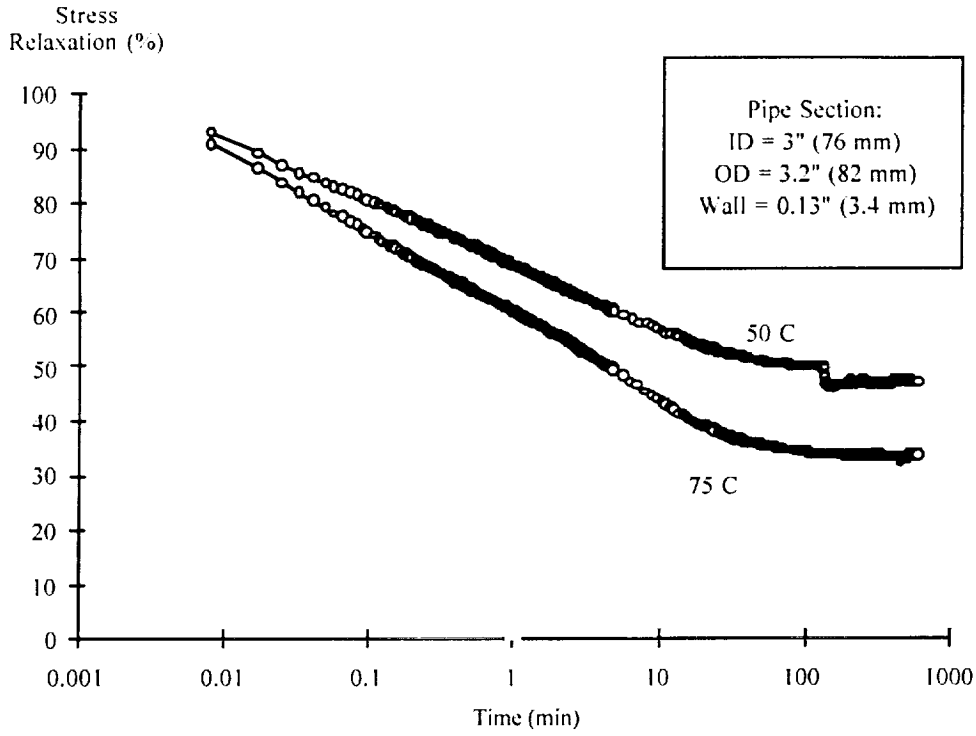

Figure 11-8. Tefzel Stress Relaxation After Two Weeks in Methanol at 65°C

Not surprisingly, because no plasticizer is present to leach out, the Tefzel specimens showed an increase in weight of 0.3% due to permeation of methanol into the polymer.

12.0 COMPUTER PROGRAM FOR ACCELERATED TESTING COMPUTATIONS

A computer program was written for construction of an accelerated test plan for thermoplastic pipe. The duty profile for the pipe is input and an activation energy is also included for the principle mode of degradation finally an acceleration factor is calculated for specific environmental exposures. We presented the program at the meeting and discussed what other exposures or information is needed from the clients to complete the computer program. The aspiration of the program is to assist the project clients in developing a comprehensive composite unit accelerated life prediction test plan based on the mission profile as well as user defined laboratory testing conditions. A complete mission profile for the thermoplastic pipe is necessary for the program. This software program upon completion will hopefully also allow the clients to forecast a commensurate age for thermoplastic pipes that have been in service and exposed to variant environmental conditions.